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Nutrient Control in Sewage Lagoons

Research Report No. 8

Vol. 1

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rch Program for the Abatement of Municipal Pollution
nder Provisions of the Canada-Ontario Agreement
on Great Lakes Water Quality

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These RESEARCH REPORTS describe the results of investigations funded under the Research Program for the Abatement of Municipal Pollution within the provisions of the Canada-Ontario Agreement on Great Lakes Water Quality. They provide a central source of information on the studies carried out in this program through in-house projects by both Environment Canada and the Ontario Ministry of the Environment, and contracts with municipalities, research institutions and industrial organizations.

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ABSTRACT

With the implementation of phosphorus removal programs in Ontario, some 80 waste treatment lagoons will require the addition of a phosphorus removal process. The most frequent proposal for accomplishing phosphorus removal has been the addition of alum or ferric chloride to the lagoon influent and subsequent precipitation of phosphates within the lagoon.

This project was initiated to provide documentation on the effects and behaviour of precipitated phosphates in sewage lagoons. Design and operational problems which might arise from chemical dosing of lagoon influents were investigated, as well as the effects of seasonal variation of temperature. The role of pH in both the removal and resolubilization of phosphorus in waste treatment lagoons was also investigated.

Two techniques were used to simulate lagoon conditions to obtain data for the possible long-term distribution of phosphates between the solid and liquid phases in treatment lagoons:

- One method utilized laboratory-scale simulators operated under closely controlled conditions of temperature and loading.
- In the second method,a computational procedure was developed, involving the use of a computer model written to simulate the removal of soluble phosphates by precipitation with alum.

Full-scale lagoons, located in Shelbourne, Ontario, were used for comparative purposes in the first method. Two laboratory units were seeded from bottom deposits, and filled with lagoon effluent taken from the full-scale lagoons. In each case one unit, or lagoon was operated as a control, and the other received chemical dosing.

In both the full-scale control lagoon and the laboratory control lagoon, it was observed that, during periods of low dissolved oxygen, both phosphorus and carbon were resolubilized from bottom deposits. The phosphorus resolubilization rate was much less dependent on temperature and lagoon maturity than carbon. Continued addition of alum to the laboratory lagoon controlled the resolubilization of phsophorus under low oxygen conditions, however, distribution of alum was not uniform enough in the full-scale lagoon to provide such control. The laboratory simulators indicated that more extensive phosphorus resolubilization would occur at higher temperatures, pH was not found to be a governing factor for phosphorus resolubilization.

The computational model did not predict similar phosphorus concentrations to those observed in the experimental data. The computer model could be perfected by extensive data correlation and parameter measurements. However, because of the many unexplained complexities of alum-phosphorus reactions in water, such an effort would not be warranted at this time.

Recommendations for further studies are presented in the final chapter.

RESUME

Avec l'application en Ontario de programmes d'élimination du phosphore, il faudra ajouter un système d'élimination du phsophore à quelque quatre-vingts bassins de traitement des déchets. La méthode de déphosphoration la plus fréquemment proposée a été l'addition d'alun ou de chlorure ferrique aux affluents du bassin et la précipitation subséquente des phsophates dans le bassin.

On a entrepris le présent travail pour accumuler de la documentation sur les effets et le comportement des phsophates précipités dans les bassins de décantation. On a étudié les problèmes de conception et d'exploitation que pourrait amener l'addition de produits chimiques aux affluents du bassin, de même que les effets des variations saisonnières de température. On a aussi étudié le rôle du pH à la fois dans l'élimination et la resolubilisation du phosphore dans les bassins de décantation.

On a utilisé deux techniques de simulation des conditions des bassins pour obtenir des données sur la distribution possible à long terme des phosphates entre les phases liquide et solide du matériel des bassins de décantation:

- La première méthode utilisait des simulateurs à l'echelle du laboratoire qui fonctionnaient dans des conditions étroitement contrôlées de température et de charge.
- Dans la deuxième méthode, on a utilisé un ordinateur; ce procédé mettait en oeuvre un modèle informatique conçu pour simuler l'élimination des phosphates solubles par la précipitation à l'alun.

Pour la première méthode, on a utilisé pour comaraison des bassins réels situés à Shelbourne (Ontario). On a ensemencé en laboratoire deux bassins à l'aide de dépôts de fonds et on les a remplis d'effluent de bassins pris des bassins réels. Dans chaque cas, un des bassins servait de témoin et l'autre recevait des produits chimiques.

Dans le bassin-témoin sur le terrain comme dans celui en laboratoire, on a observé que, au cours des périodes où il y avait peu d'oxygène dissous, le phosphore et le carbone étaient resolubilisés par

dépôts de fonds. Le taux de resolubilisation du phosphore dépendait coup moins de la température et de la maturité du bassin que du carbone. dition continuelle d'alun au bassin du laboratoire a empêché la lubilisation du phosphore dans les conditions de faible teneur en ène, mais la distribution de l'alun n'a pas été assez uniforme dans ssin sur le terrain pour donner un tel rèsultat. Les simulateurs boratoire ont indiqué qu'il se produirait une resolubilisation plus tante du phosphore aux températures élevées; on a trouvé que le 'était pas un facteur déterminant dans la resolubilisation du phosphore.

Le modèle informatique n'a pas prédit de concentrations de hore similaires à celles qu'on a obtenues dans les expériences. odèle pourrait être perfectionné par des corrélations de données et nesures de paramètre. Cependant, à cause des nombreuses complixités liquées des réactions alun-phosphore dans l'eau, un tel effort ne t pas justifié pour le moment.

On trouvera dans le chapitre final des recommandations portant es études supplémentaires à exécuter.

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Chapter 1

INTRODUCTION

With the implementation of phosphorus removal programs in Ontario, some 80 waste treatment lagoons will require the addition of a phosphorus removal process. The most frequent proposal for accomplishing phosphorus removal has been the addition of alum or ferric chloride to the lagoon influent and subsequent precipitation of phosphates within the lagoon.

Normal operation of a sewage lagoon requires the separation of liquids and solids as well as biological reactions in both phases. Under favourable conditions of temperature, solids deposited on the bottom are known to under-go anaerobic degradation. This project was initiated to discover whether or not precipitated phosphates will be resolubilized into the effluent as a result of pH changes or anaerobic activity in the bottom deposits of waste treatment lagoons.

This interim report covers the results and interpretations of our observations up to mid-March, 1973.

1.1 Purpose

The purpose of this project was to provide documentation on the effects of precipitated phosphates in sewage lagoons. Under normal circumstances, this information could have been obtained by observing a full-scale test lagoon over an extended period of time. Due to the seasonal variation in normal lagoon activity and the temperature extremes experienced in Ontario, such a program would probably require a duration of at least two or three years. However, many of the lagoons will have required implementation of a phosphorus removal process prior to that time. Therefore, some other method had to be used in order to determine possible design or operational problems that might arise from chemical dosing of lagoon influents.

This project used two techniques for simulation of lagoon conditions in order to obtain data on the possible long-term distribution of phosphates between the solids and liquids in treatment lagoons:

1. One method utilized laboratory-scale simulators of lagoons operated under closely controlled conditions of temperature and loading.

2. The second method was based on chemical equilibrium calculations to determine the stoichiometry for 43 possible reactions of 12 common ions in natural water. These calculations utilize solubility co-efficients for the various reaction products, in order to predict the distribution of phosphates between solids and liquids.

1.2 Scope

The scope of this study included:

- Estimation of the influence of bottom deposits and precipitated phosphorus on the performance of sewage lagoons using chemical treatment for phosphorus removal.
- Investigation of the effects of temperature on both the biological and chemical processes in a typical sewage lagoon.
- Evaluation of the role of pH on both the removal and resolublization of phosphorus in the lagoon.

Chapter 2

LABORATORY SIMULATIONS OF WASTE TREATMENT LAGOONS

The laboratory simulators were operated in order to observe the effect of temperature and chemical dosing on a typical sewage lagoon. This was accomplished by operating both a control lagoon and a chemically-dosed lagoon under cold weather and warm weather conditions. Provisions were made to alternate each pair of simulators from cold weather to warm weather several times in order to simulate seasonal variations in temperature as experienced in a normal lagoon. Utilizing this technique, it is possible to simulate an entire year's operation of a typical lagoon in approximately four months.

2.1 Procedure

A schematic diagram of the laboratory simulators is shown in Figure 1, Appendix I. Whereas full-scale lagoons rely on surface aeration and photosynthetic activity of algae to provide oxygen to the process, these mechanisms cannot be readily duplicated in the laboratory. Instead, oxygen was provided to the laboratory units by a sparger system at appropriately minimal air flow rates.

The full-scale lagoon used for comparative purposes on this project was located in Shelbourne, Ontario. The process consisted of two cells in parallel, where one cell was treated with alum by application to the influent and the other remained as a control. The laboratory units were seeded with bottom deposits from the lagoons and filled with lagoon effluent. Two laboratory units were set up, using material from each of the lagoons in Shelbourne.

One pair of simulators, consisting of a chemically-treated unit and a control unit, was then placed in operation in a temperature-controlled room at approximately $5^{o}C$. The other pair of units was operated at ambient temperature in the laboratory at approximately $23^{o}C$. All of these lagoon simulators were operated with a nominal residence time of 80 days. Shelbourne sewage was used for feeding the simulated lagoons daily. Five times per week, 200 mg/l of alum was added to the influent sewage to simulate the chemically-treated operation. The alum and sewage were subjected to a rapid mix for two minutes prior to addition to the laboratory units.

Samples were taken from each lagoon simulator once weekly from both the top and bottom sampling points. Each sample was analysed for total phosphorus, BOD and pH. Ortho phosphorus and total soluble phosphorus were measured periodically. Dissolved oxygen measurements were taken at mid-depth in the units.

An acclimatization period of four weeks was provided before sampling and analytical determinations began, with the exception that effluent BOD was measured in the third and fourth weeks.

2.2 Results and Inferences

Phosphorus removal during the first complete seasonal cycle is shown on Figure 2. Phosphorus concentration in the raw feed and residual phosphorus in the effluent are shown for the treated unit in Figure 3 and the control unit in Figure 4. Figure 5 shows a probability distribution of phosphorus removal performance for both the control and chemically-treated units under both cold and ambient conditions. The distribution of residual phosphorus in the effluents from all simulators is indicated in Figure 6.

The results shown in Figures 2 - 6 indicate that:

1. Over a period of 21 weeks, the chemically-treated units showed a consistent performance throughout, while over the same period, the effluent from the control units showed a continuing decline in performance.
2. The results of phosphorus measurements taken from both the top and bottom sampling points in each of the units indicated only marginal differences. Since it appeared that the small amount of air supplied to the unit was sufficient to mix the entire contents, the sampling routine was limited to top samples only, except when experimental procedures were used which involved cutting off the air supply.
3. Numerous measurements were taken of both ortho phosphorus and total soluble phosphorus and compared with total phosphorus. Only marginal differences were observed, and therefore total phosphorus was used as the regular monitoring parameter.

4. Measurements of pH, taken throughout the study on all laboratory units, showed neither significant changes nor detectable trends. Observed pH values ranged randomly from 7.7 to 8.2.

5. Measurements of dissolved oxygen indicated levels near saturation for most of the time. The lowest measurements recorded during the period when air was supplied to the units, were 4.1 mg/l for the ambient unit and 8.1 for the cold unit.

6. Effluent BOD values for each of the laboratory units are shown on Figure 7. These values indicate that after several weeks of operation, a stabilized effluent BOD of less than 10 mg/l was obtained.

7. In order to evaluate the possible effect of the relatively high oxygen levels maintained in the laboratory units, all units were operated without aeration for a period of two weeks. Figure 8 shows the depletion of dissolved oxygen in the lagoon simulators. Concentrations of total phosphorus at both the top and bottom of each unit were monitored daily and are shown in Figures 9 and 10, respectively. These results indicated no detectable difference in phosphorus concentration for the chemically-treated simulators at either temperature. However, there appeared to be a definite trend of increasing phosphorus concentration for both control units. It should be noted as well that the increase in total phosphorus was more apparent for the lower depth samples than for the surface samples. No significant changes in pH or BOD were observed during this two-week period.

2.3 Comparison of Laboratory Results With Full-Scale Observations

Since the purpose of this project was to simulate lagoon behaviour with respect to phosphorus effects, there was no particular necessity to show comparisons of BOD removal from both systems. However, it was important that the laboratory units demonstrated sufficient anaerobic degradation in the bottom deposits (as evidenced by a feedback of soluble BOD to a full-scale lagoon) to determine the effect of this condition on precipitated phosphorus. The higher BOD observed in the full-scale lagoons, when compared with the laboratory units, may have reflected only the relative amounts of bottom deposits per volume of liquid and the maturity of the full-scale system. Further, the greater oxygen source near the bottom of the laboratory units assisted in providing a lower BOD level in the final effluent under cold weather operation. The greater degree of mixing achieved in the laboratory units may also have influenced the BOD removal in these units.

Figure 11 shows the results of dissolved oxygen and temperature measurements taken during our on-site inspections at Shelbourne. Similarly, pH and effluent phosphorus concentrations are shown on Figure 12.

The average pH values and average monthly phosphorus concentrations in both raw sewage and effluent from both the control and the chemically-treated units are shown on Figure 13. These data summarize measurements collected by the Ontario Ministry of the Environment between April, 1971 and August, 1972.

The graph on Figure 11 shows that the available oxygen in the system decreased as the temperature decreased. Algal activity was severely curtailed. At the same time, pH was reduced and phosphorus was leached at an increased rate. It was observed at both the full-scale and the laboratory unit that continuous addition of alum minimized the reappearance of phosphorus. The slight increase in effluent phosphorus concentration from the treated full-scale lagoon under cold weather conditions may be explained by the unequal distribution of alum sludge across the bottom of the 6.6 acre pond. Hence, the laboratory unit, with a uniform level of alum on the bottom deposits, showed no significant resolubilization of phosphorus in the surface liquid. The laboratory units did not show any significant changes in pH as compared with the field observation even when the units were operated for two weeks with no oxygen supply. This observation may have merely illustrated that a two-week period of decreased oxygen supply was insufficient to simulate the true effects of field conditions during ice cover. It should be noted, however, that even this two-week period of low oxygen was sufficient to produce phosphorus leaching. As a result of these preliminary observations on the effect of low oxygen levels, further experimental work is planned to document the information obtained to date. Specific details of the programs planned are shown in Chaper 5 (Recommendations).

Chapter 3

CHEMICAL EQUILIBRIUM COMPUTATIONS

3.1 Approach

A computational procedure was developed for determining the probable compounds formed from several common ions in water.

It involved a computor model, written to simulate the removal of soluble phosphates by precipitation with alum. This model was based on the premise that the numerous precipitation and complex-ion-formation reactions occur simultaneously and at equilibrium. The reactions selected were:

- reactions involving those cations and anions thought to influence alum solubility and which are currently being monitored as criteria of water quality;
- reactions and associated equilibrium constants currently documented in the literature; and,
- reactions resulting in the formation of solids which earlier studies have shown to exist in an aqueous ionic environment similar to wastewater (1).

In the initial stage of work, two objectives were set:

1. To determine which of the solid phases of aluminum were the most thermodynamically stable under various initial conditions.
2. To determine if an equilibrium model based on data from the literature could be used to predict the extent of phosphorus removal occurring in a typical wastewater undergoing alum treatment.

The first objective was met. Variscite was found to be the stable solid phase below a pH value of 7.25; gibbsite the stable phase in solutions of pH greater than 7.25. The equilibrium model based on literature data was not a realistic representation of phosphorus removal as observed experimentally.

In the second stage, the basic model structure (i.e. the proposed set of reactions) was retained, but it was intended to determine if values of the equilibrium constants could be found which would permit the equilibrium model to be used in the prediction of phosphorus removal. The equilibrium constants of particular interest were the solubility products of aluminum hydroxide and aluminum phosphate. This stage of the work was partially successful.

Twelve anions and cations were selected as the basic components of the reactions used in the model, as follows:

ANIONS	OH^-	PO_4^{3-}	CO_3^{2-}	SO_4^{2-}	F^-	Cl^-
CATIONS	H^+	Al^{3+}	Ca^{2+}	Mg^{2+}	K^+	Na^+

These components were considered to participate with one another in forty-three different reactions, forty-one in the liquid phase, two in the solid phase.

The reactions were classified as follows:

a. Reactions of anions with the hydrogen ion, commonly referred to as acid dissociations.

ANION	No. Reactions	Products
PO_4^{3-}	3	H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}
SO_4^-	1	HSO_4^-
F^-	2	HF, H_2F^+
CO_3^{2-}	2	HCO_3^-, H_2CO_3
OH^-	1	H_2O

b. Hydroxide complexes - hydrolysis reactions

CATION	No. Reactions	Products
Ca^{2+}	1	$CaOH^-$
Mg^{2+}	1	$MgOH^-$
Al^{3+}	6	$AlOH^{-2}$, $AlOH_2^-$, $AlOH_4^+$, $Al_2OH_2^{-4}$, $Al_7OH_{17}^{-4}$, $Al_{13}OH_{34}^{-5}$

c. Sulphate ionic complexes

CATION	No. Reactions	Products
Al^{3+}	2	$AlSO_4^+$, $Al(SO_4)_2^-$
Ca^{2+}	1	$CaSO_4$
Mg^{2+}	1	$MgSO_4$
Na^+	1	$NaSO_4^-$
K^+	1	KSO_4^-
		$Al(SO_4)_2^-$

d. Fluoride complexes

CATION	No. Reactions	Products
Mg^{2+}	1	MgF^+
Ca^{2+}	1	CaF^+
Al^{3+}	6	AlF^{2+}, AlF_2^+, AlF_3, AlF_4^-, AlF_5^{2-}, AlF_6^{3-}

e. Carbonate complexes

CATION	No. Reactions	Products
Mg^{2+}	2	$MgCO_3$, $MgHCO_3^+$
Ca^{2+}	2	$CaCO_3$, $CaHCO_3^-$
Na^+	2	$NaCO_3$, $NaHCO_3^-$

f. Phosphate complexes

CATION	No. Reactions	Products
Mg^{2+}	1	$MgHPO_4$
Ca^{2+}	3	$CaPO_4^-$, $CaHPO_4$, $CaH_2PO_4^+$

g. Formation of solid phases

Variscite - $AlPO_4$

Gibbsite - $Al(OH)_3$

Each reaction set has a particular significance in describing the chemical state of the liquid phase. The acid dissociation reactions describe the buffering capacity of the liquid phase. The formation of ion complexes results in increased solubility of the metal ions by decreasing the availability of the free metal ions for precipitation. The partition of aluminum between the two solid phases, and thus the efficiency of phosphate removal, is described by the solubility product equations for variscite and gibbsite. The details for the use of the computer program and methods for calculation of these 4 proposed species are given in Appendix II.

3.2 Results and Discussion

The initial evaluation was done on the results collected by the Ontario Ministry of the Environment for Shelbourne Sewage Lagoon over the period May '71 to July, 1972. The initial concentrations of the ion components were set at averages estimated from influent data during this period. The mean and standard deviations are shown below:

ION COMPONENT	AVERAGE (mg/1)	STANDARD DEVIATION
SO_4^{-2}	53.9	19
Ca^{+2}	64.5	11.4
Mg^{2+}	25.4	5.9
K^+	10.0	2.3
Na^+	58.4	8.5
Cl^-	60.4	13.4
Hardness	345.1	47.3
Alkalinity	278.1	71

The alkalinity was assumed to be representative of the inorganic concentration. Initial phosphate concentrations of 55.2, 42.9, and 30.7 mg PO_4/1 were considered, as well as initial alum dosages of 200, 150 mg/1 ($Al_2(SO_4)_3 \cdot 14H_2O$). The residual aluminum and phosphate concentrations were calculated at these initial loadings over a pH range of 4 to 8. The total fluoride ion concentration was assumed to be 1 mg/1.

The calculated phosphorus and aluminum residuals are shown in Figures 4 to 19. These results indicate that, for an aqueous solution with a hydrogen ion concentration less than pH = 7.25, variscite (aluminum phosphate) is the stable phase. Above this pH value, gibbsite becomes the stable phase in equilibrium. If the solubility products as taken from the literature are a true indication of the solubility of each phase, then gibbsite would be the final solid phase formed in the lagoon effluent (as the sample pH is normally above 7) at equilibrium.

On Figure 20, the residual phosphate concentration as measured in a wastewater effluent from the Acton Water Pollution Control Plant is shown. The wastewater sample initially contained 29 mg PO_4/1 to which an alum dosage of 15 mg Al^{+3}/1 was added. On comparison of this figure to the previous set, it becomes apparent that the equilibrium model predictions of phosphorus removal do not follow the same trends as observed experimentally.

First, removal of phosphorus with alum is observed to occur at higher solution pH values (i.e. pH values approaching 8). It is believed that the removal of phosphates after a pH value of 8 is due not to alum precipitation but precipitation of phosphates with calcium occurring naturally in the wastewater.

Secondly, the removal of phosphates at pH values between 4 and 7 is less than that of the model predictions (i.e. the model residual curve is flat in this pH range).

The reasons for these deviations between the observed and predicted removal are as follows:

- The model fails to predict phosphate removal at pH values approaching 8 because the relative magnitude of the solubility product for aluminum phosphate is too small in comparison to aluminum hydroxide. No removal is predicted by the model for pH values greater than 8 as calcium precipitation was not initially considered.
- At the low pH range of 4 to 7, the low removal observed, as compared to the model predictions, indicates that a soluble complex of the type AlH_2PO_4 or $AlHPO_4$ exists in this pH range. Such complexes have been reported in the literature to exist but good estimates of the equilibrium constants for these reactions are unavailable. Improving the predictive ability of the model became the objective of the second stage of the computational procedure. It was felt that the model predictions could be improved by readjusting the values of the solubility products for aluminum hydroxide and phosphate.

Experimental data were obtained for the efficiency of phosphorus removal by alum in a sample of influent taken from the waste stabilization lagoon at Shelbourne over the pH range of interest. Additional details of the procedure are given in Appendix II.

Figure 21 shows a comparison of the revised model with experimental data. Note again a particular anomaly of the model is the extremely low residual concentrations predicted at the acidic conditions of pH 6 to 7.

Since the experiments showed a higher residual concentration, it must be concluded that an aluminum phosphate complex (probably AlH_2PO_4) was being formed under these conditions and increasing the solubility. The equilibrium constant for such a reaction could be considered as a fifth search parameter, but a reasonable estimate of the magnitude of such a complex was not found in the literature. Thus, the choice of a starting value would have to be intuitive.

As a final step, the model was reconstructed with the original reaction sets (with the exception of the extra hydroxy-apatite and calcite). The value of the solubility products for these solid phases were taken from the studies of Ferguson and McCarty (2). The ion component concentrations were set at levels used in the first study. Alum dosages of 200 and 250 mg/1 $Al_2(SO_4)_3 \cdot 14H_2O$ were tested against an initial phosphate concentration of 30.4 mg/1.

The predicted phosphate and aluminum residual concentrations are shown over a pH range of 6 to 10, on Figures 22 and 23, respectively.

Chapter 4

CONCLUSIONS

The following conclusions were drawn on the basis of the experiments and calculations described in this report:

1. Observations on both the full-scale control lagoon and the laboratory lagoon showed that, during periods of low dissolved oxygen, both phosphorus and carbon were resolubilized from the bottom deposits. However, the phosphorus resolubilization rate was much less dependent on temperature and lagoon maturity than carbon.

2. Continued addition of alum to the laboratory lagoon controlled the resolubilization of phosphorus under low oxygen conditions.

3. The limited amount of field data available indicates that the resolubilization of phosphorus is considerably controlled by alum addition but that the distribution of alum is not uniform enough to provide control over the entire lagoon area.

4. The laboratory simulators indicated that more extensive phosphorus resolubilization would occur at higher temperatures. Hence, when alum was added to control phosphorus resolubilization, the performance of the 5°C simulator was marginally better than the warmer unit. Decreases in pH were observed in both the full-scale lagoons. However, since phosphorus was resolubilized in one case, but controlled by chemical addition in the other, it was concluded that the lowering of pH alone was not the governing criterion for phosphorus resolubilization.

5. The computational model which calculates the stoichiometry of various simultaneous chemical reaction did not predict similar phosphorus concentrations to those observed in the experimental data. The actual phosphorus removal process in natural waters is a combination of many complex chemical and physical phenomena which cannot be described by simple chemical reactions.

6. The computer model could be perfected by extensive data

correlation and parameter measurements. However, because of the many unexplained complexities of alum-phosphorus reactions in natural waters such an effort would not be warranted at this time.

Chapter 5

RECOMMENDATIONS

On the basis of the observations made to date and the conclusions as presented, we recommend that this program continue in the following manner:

1. The present program should be continued at least until October, 1973, in order to obtain an additional $1\frac{1}{2}$ to 2 sets of seasonal cycles.

2. All of the units should be operated without an air supply for at least $\frac{1}{2}$ of a seasonal cycle and both top and bottom samples should be taken, in order to confirm phosphorus leaching data.

3. One of the control lagoons should be converted to 200 mg/l of alum addition, in order to obtain observations on start-up performance. On the basis of phosphorus out-put concentrations obtained in the period from March '73 to June '73, chemical dosages should be adjusted commencing in July, 1973. Thus, observations can be obtained on the effect of such changes on the effluent quality.

4. In view of the inability of the stoichiometric model to predict full-scale observations without major revisions to the parameter estimates, the intended program of predicting the performance of the laboratory units should not proceed.

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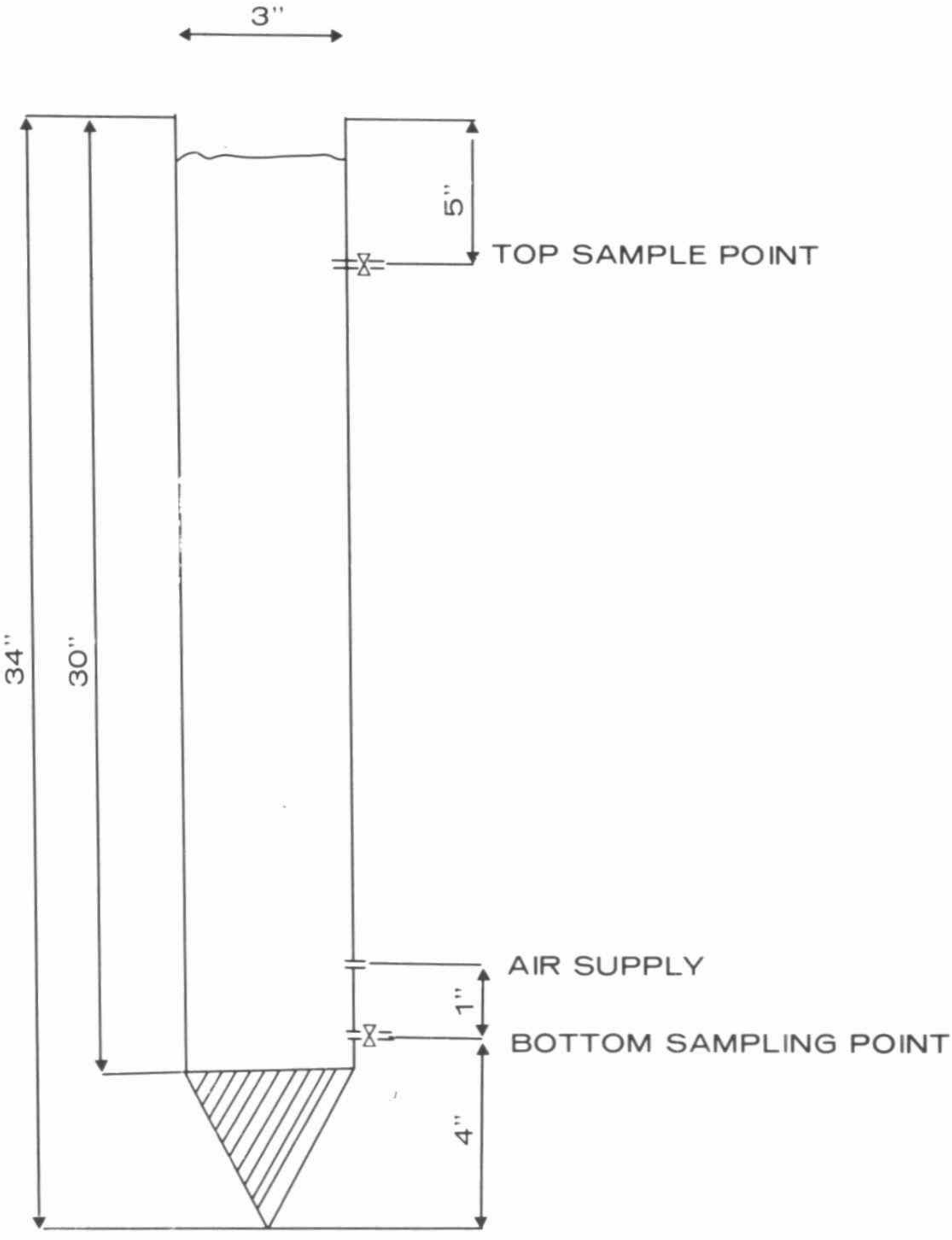
ABBREVIATIONS

BOD	biochemical oxygen demand
^oC	degrees Centigrade
mg/l	milligrams per litre
OME	Ontario Ministry of the Environment
ppm	parts per million
WPCP	water pollution control plant
Al	aluminum
C	carbon
Ca	calcium
Cl	chlorine
F	fluorine
H	hydrogen
K	potassium
Mg	magnesium
Na	sodium
O	oxygen
P	phosphorus
S	sulphur

APPENDIX I

FIGURES

FIGURE 1. SCHEMATIC DIAGRAM OF LABORATORY SIMULATOR



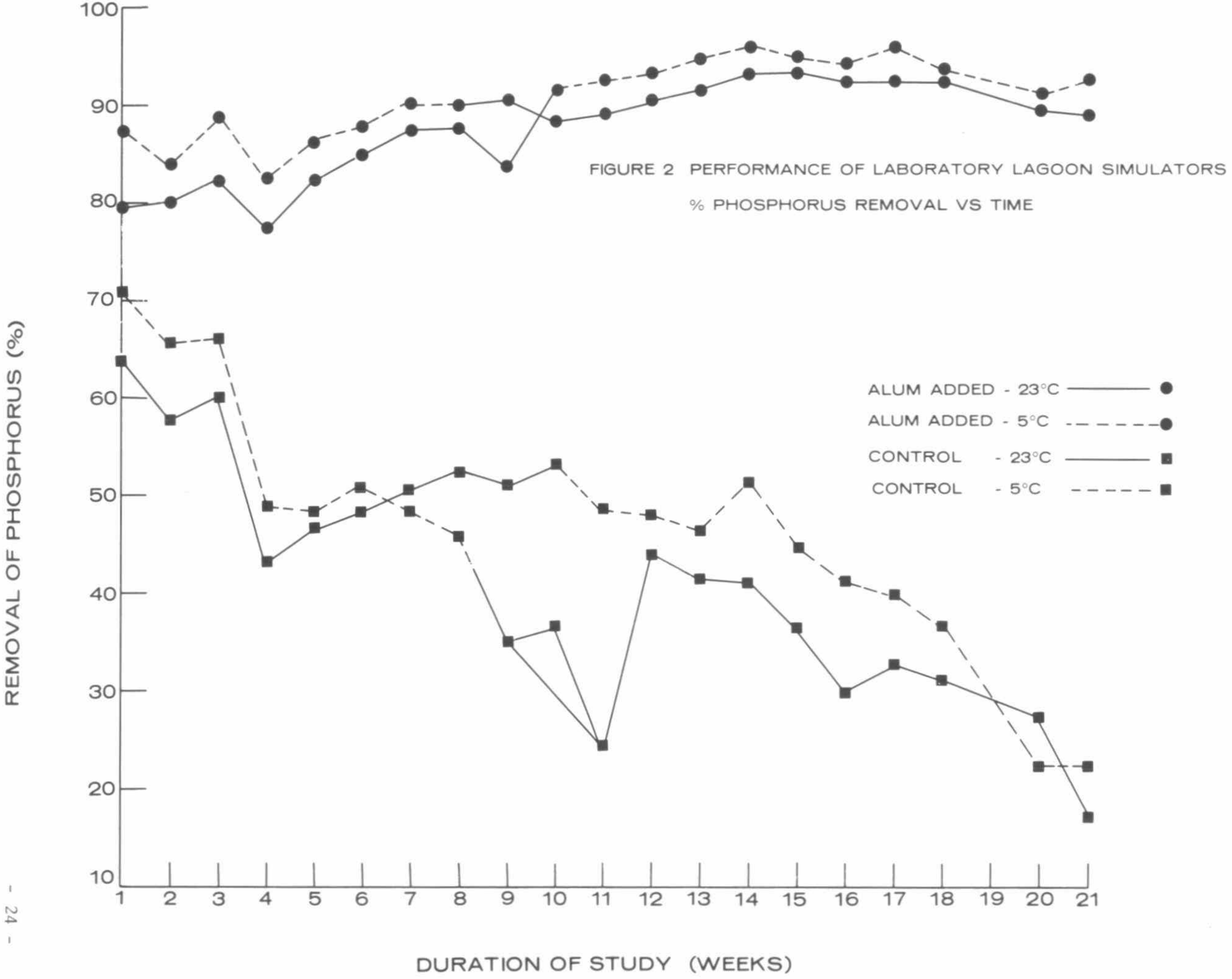
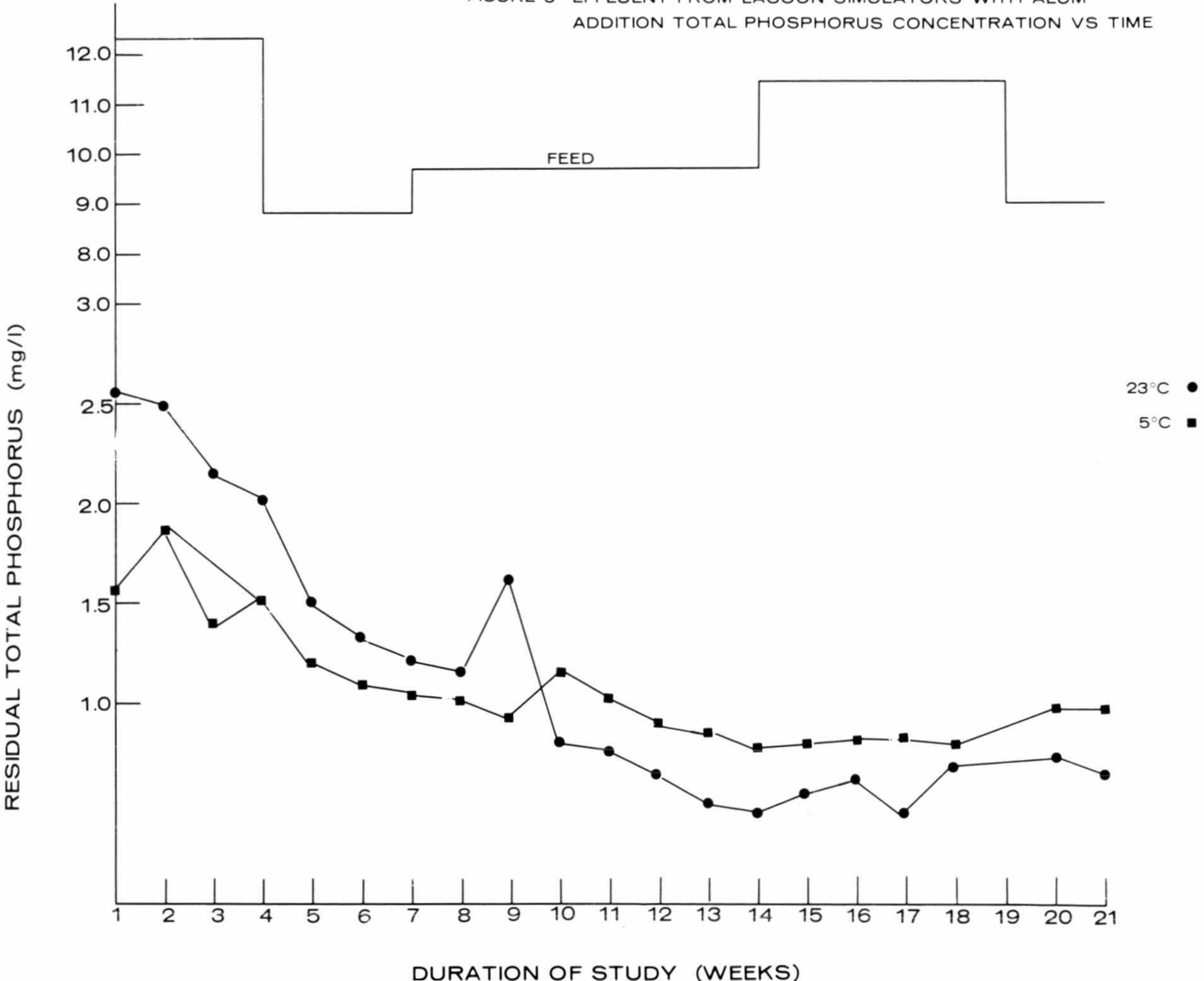


FIGURE 2 PERFORMANCE OF LABORATORY LAGOON SIMULATORS

% PHOSPHORUS REMOVAL VS TIME

FIGURE 3 EFFLUENT FROM LAGOON SIMULATORS WITH ALUM ADDITION TOTAL PHOSPHORUS CONCENTRATION VS TIME



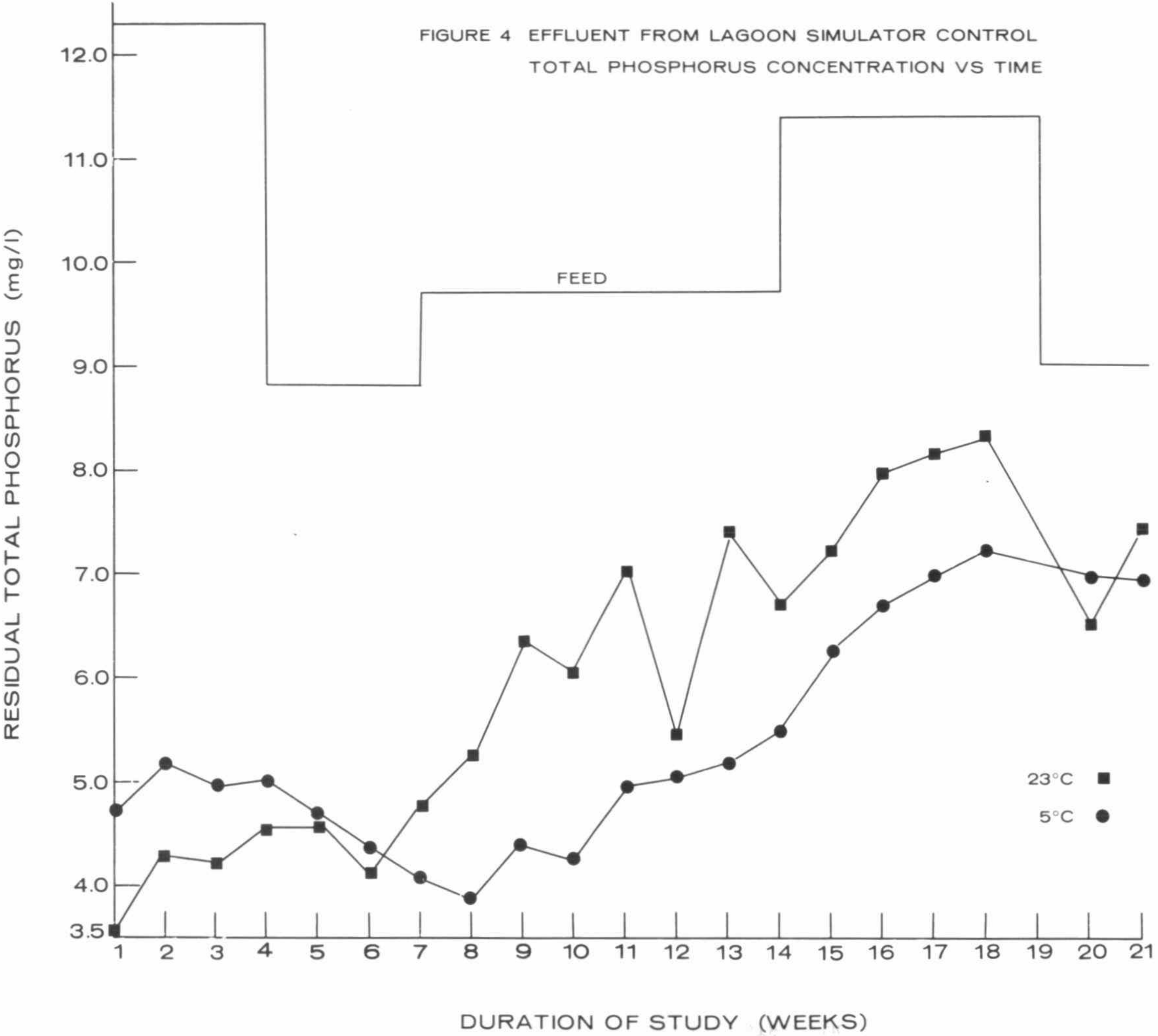


FIGURE 4 EFFLUENT FROM LAGOON SIMULATOR CONTROL TOTAL PHOSPHORUS CONCENTRATION VS TIME

FIGURE 5 DISTRIBUTION OF PHOSPHORUS REMOVAL PERFORMANCE IN LABORATORY LAGOON SIMULATORS

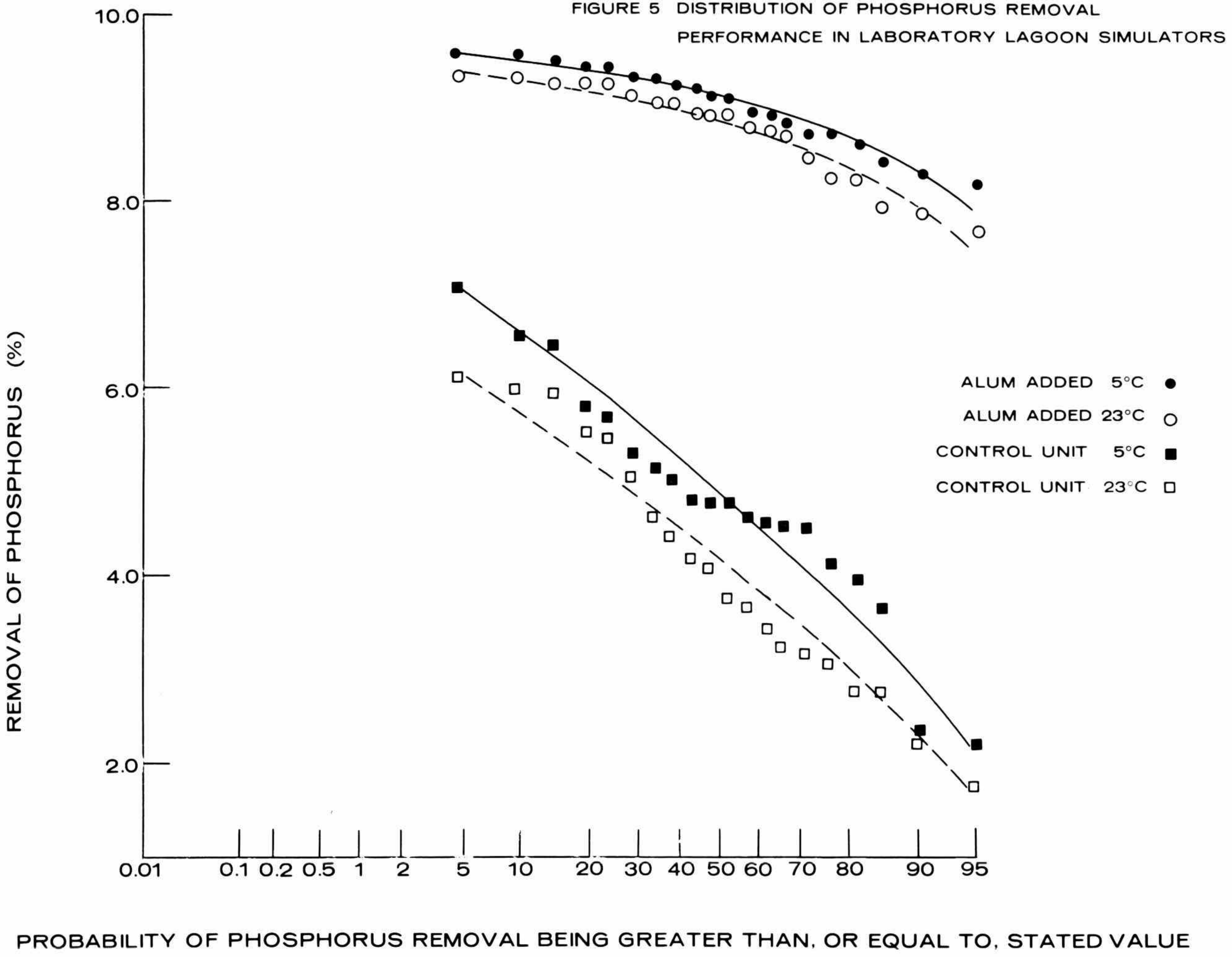


FIGURE 6 DISTRIBUTION OF RESIDUAL PHOSPHORUS IN EFFLUENTS FROM LABORATORY LAGOON SIMULATORS

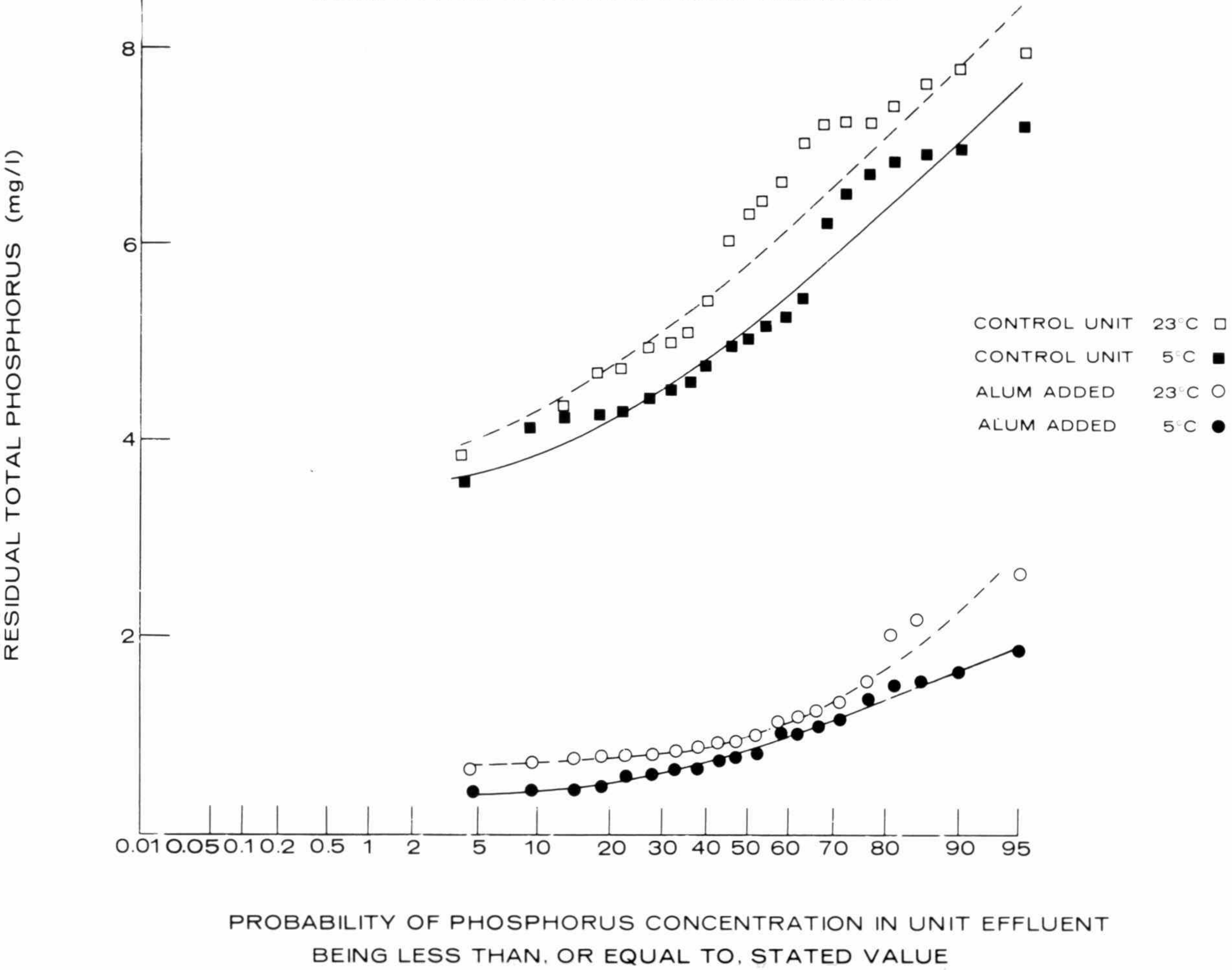


FIGURE 7 BOD CONCENTRATION IN EFFLUENTS FROM LABORATORY LAGOON SIMULATORS

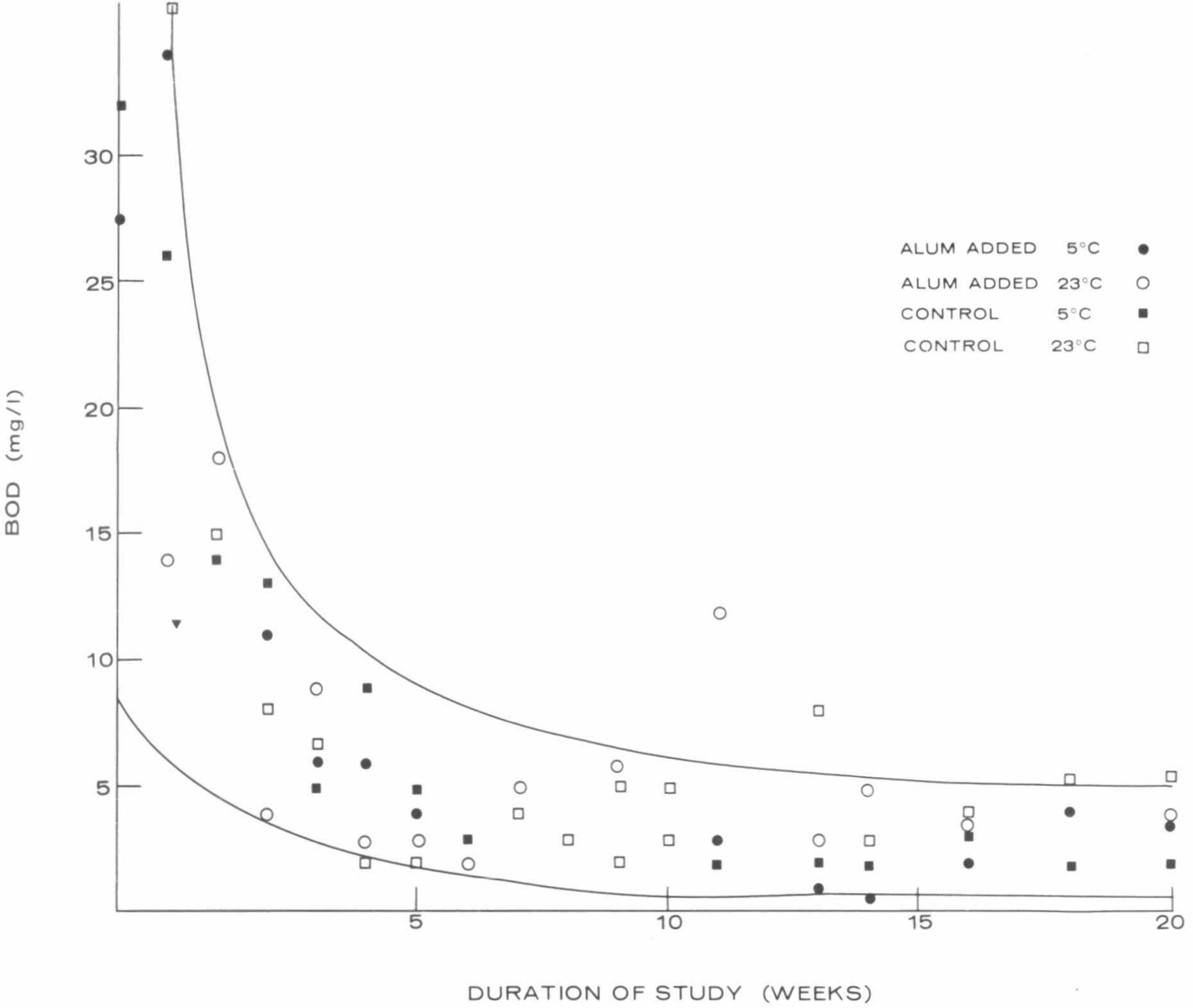


FIGURE 8 DEPLETION OF OXYGEN N IN LAGOON SIMULATORS WITHOUT AERATION

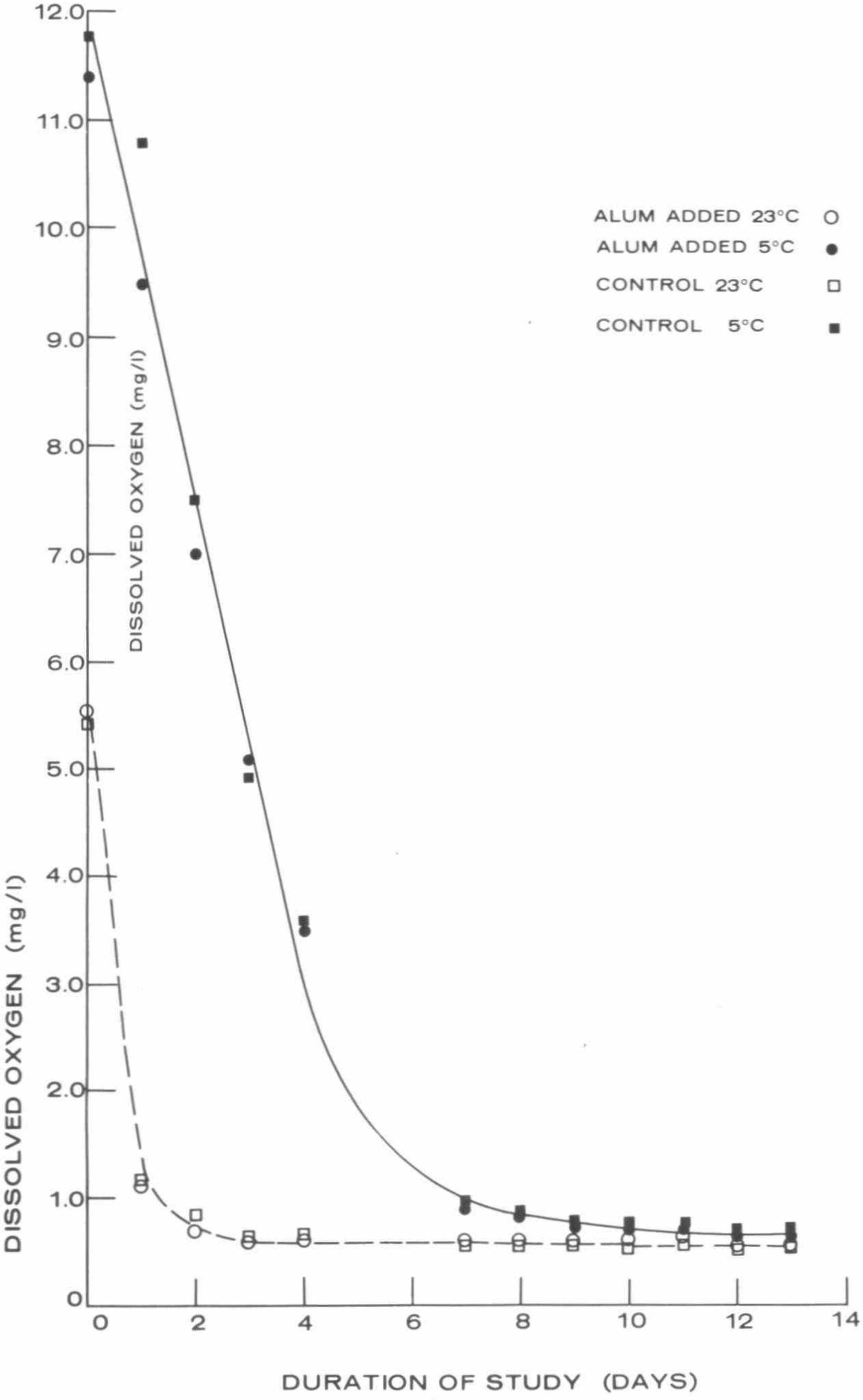


FIGURE 9 PHOSPHORUS CONCENTRATION AT THE TOP OF SIMULATORS DURING THE PERIOD WITHOUT AERATION

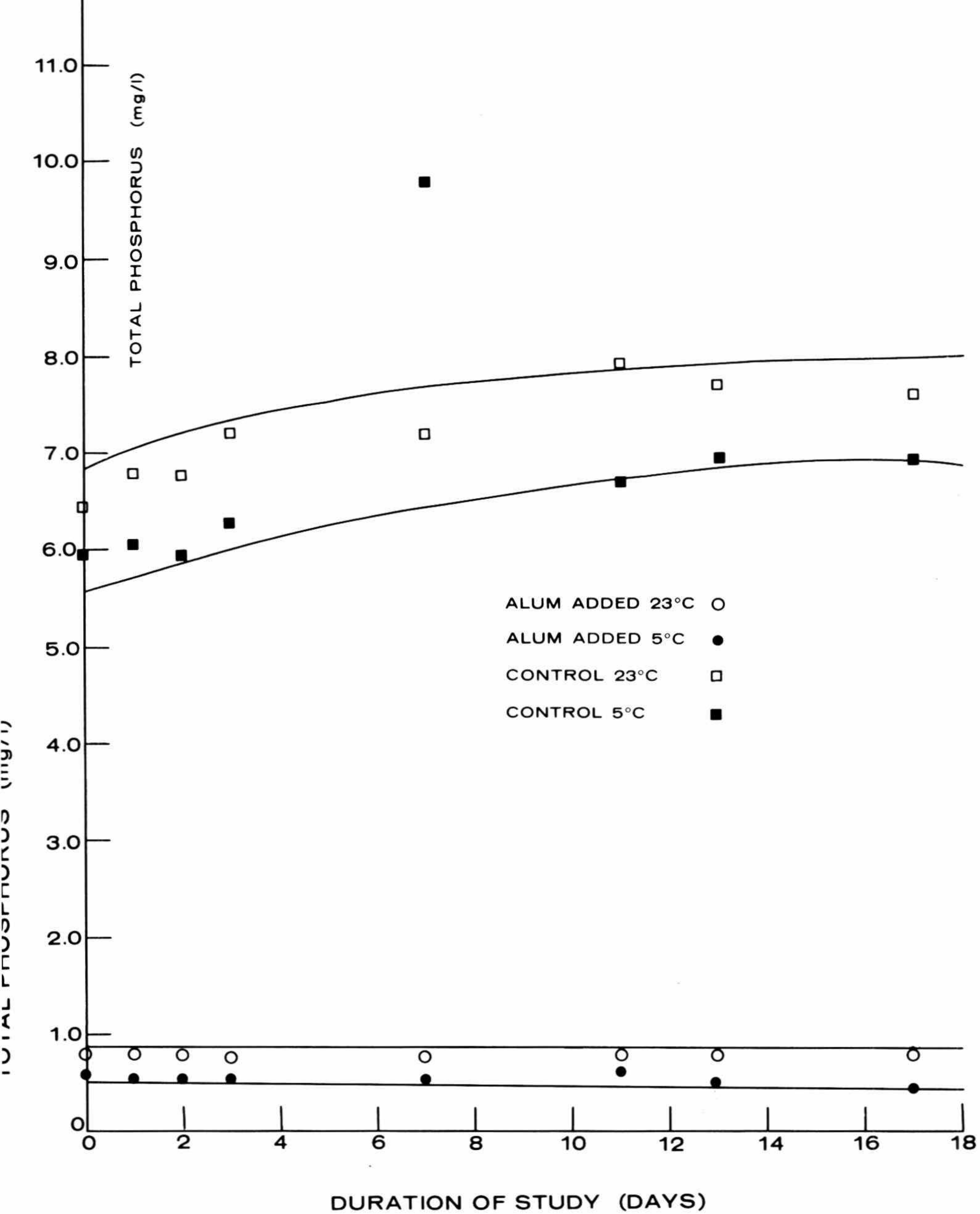


FIGURE 10 PHOSPHORUS CONCENTRATIONS AT BOTTOM OF SIMULATORS DURING THE PERIOD WITHOUT AERATION

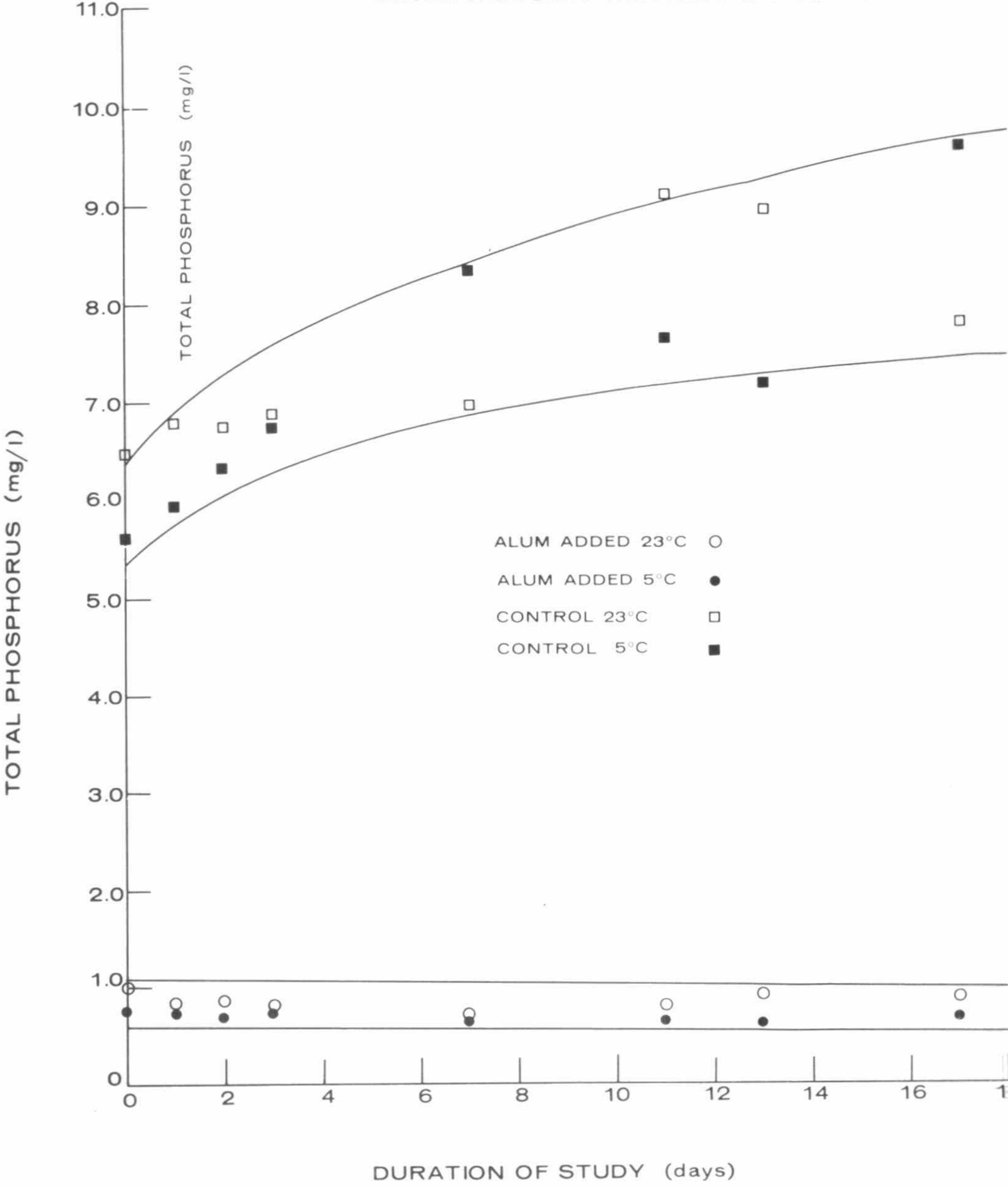


FIGURE 11 TEMPERATURE AND DISSOLVED OXYGEN VARIATION IN FULL-SCALE LAGOONS AT SHELBOURNE (MEASURED BY POLLUTECH)

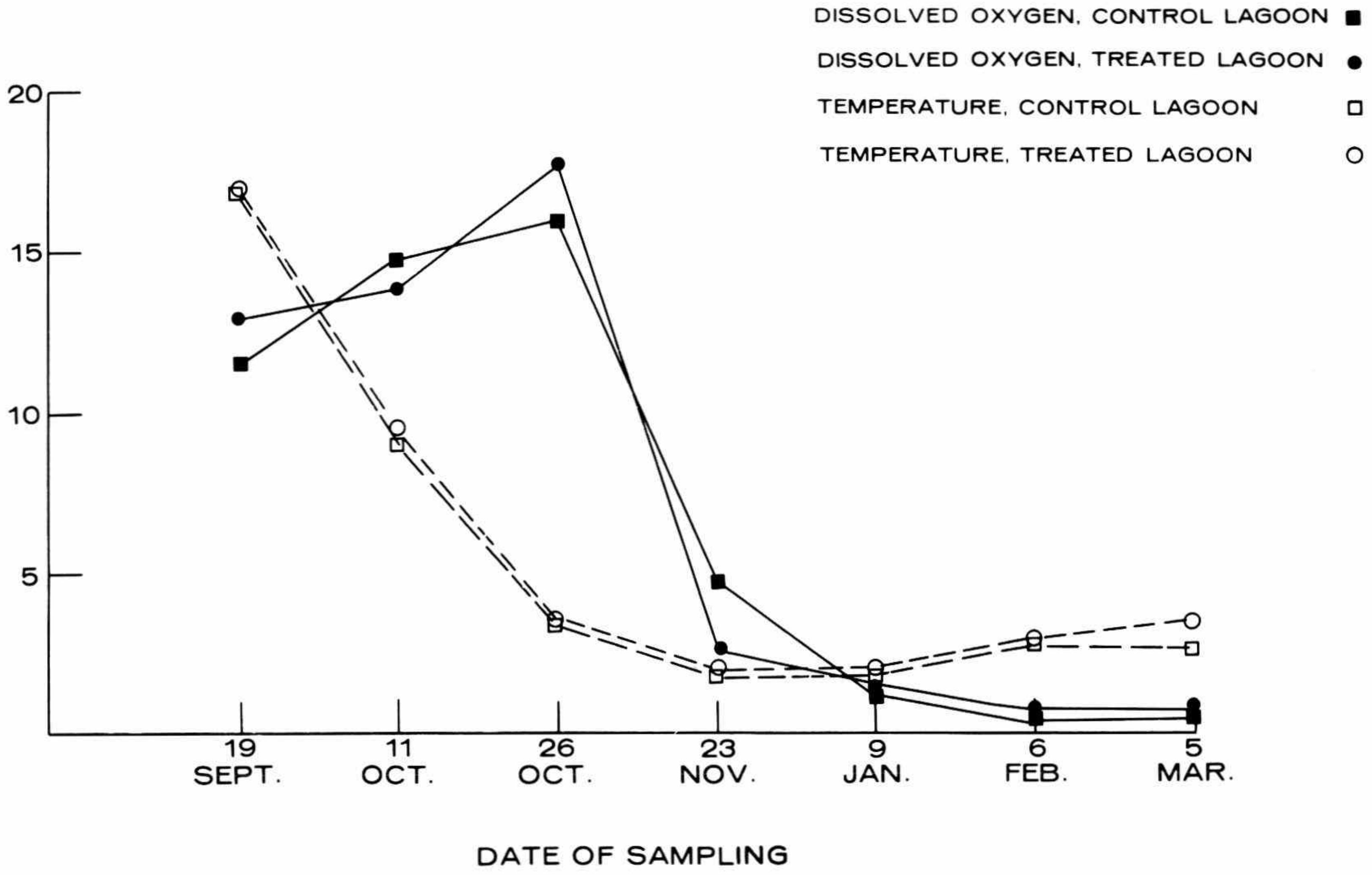


FIGURE 12 CONCENTRATION OF EFFLUENT pH AND TOTAL PHOSPHORUS

(MONITORED AT SHELBOURNE BY POLLUTECH)

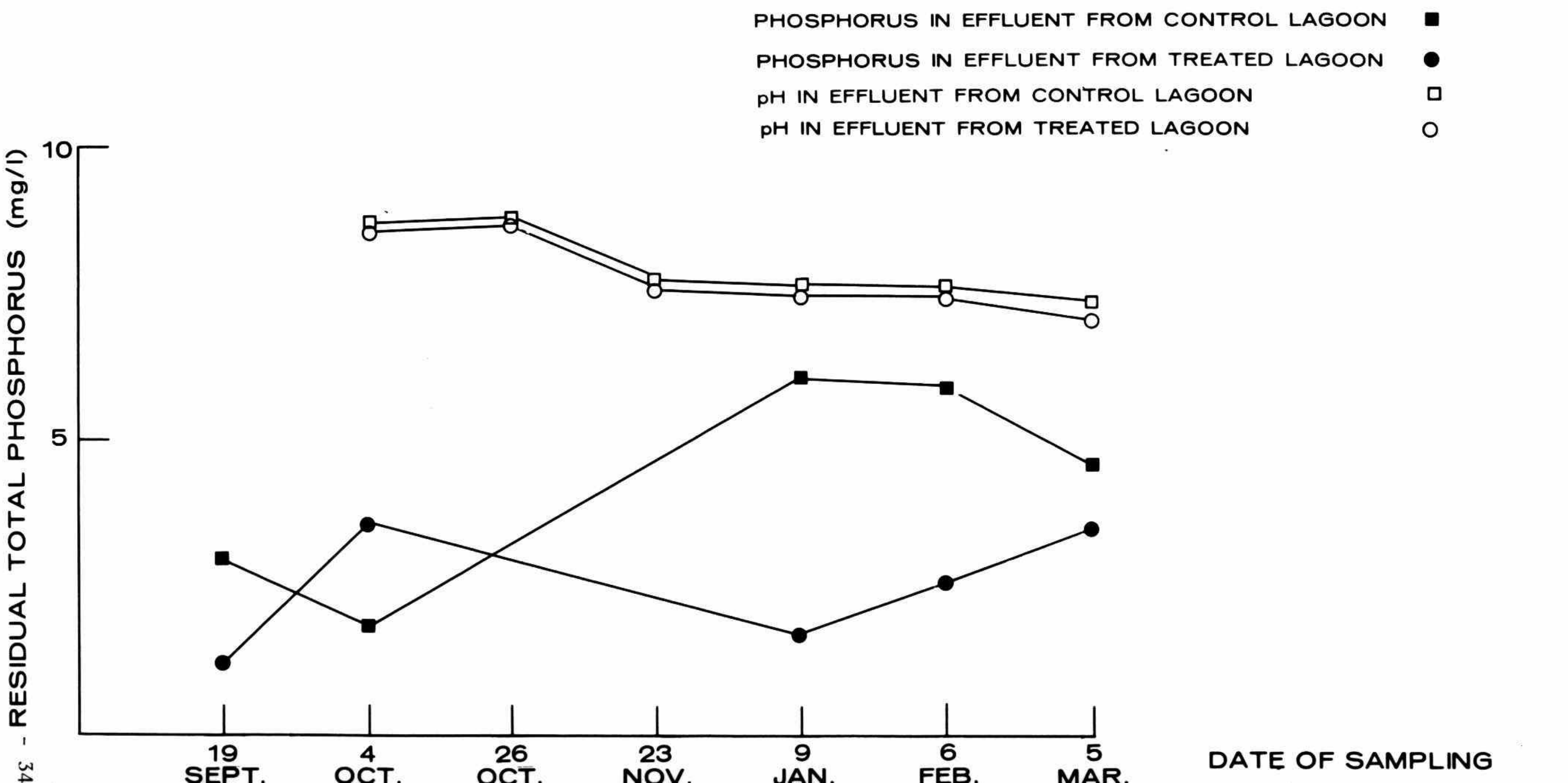
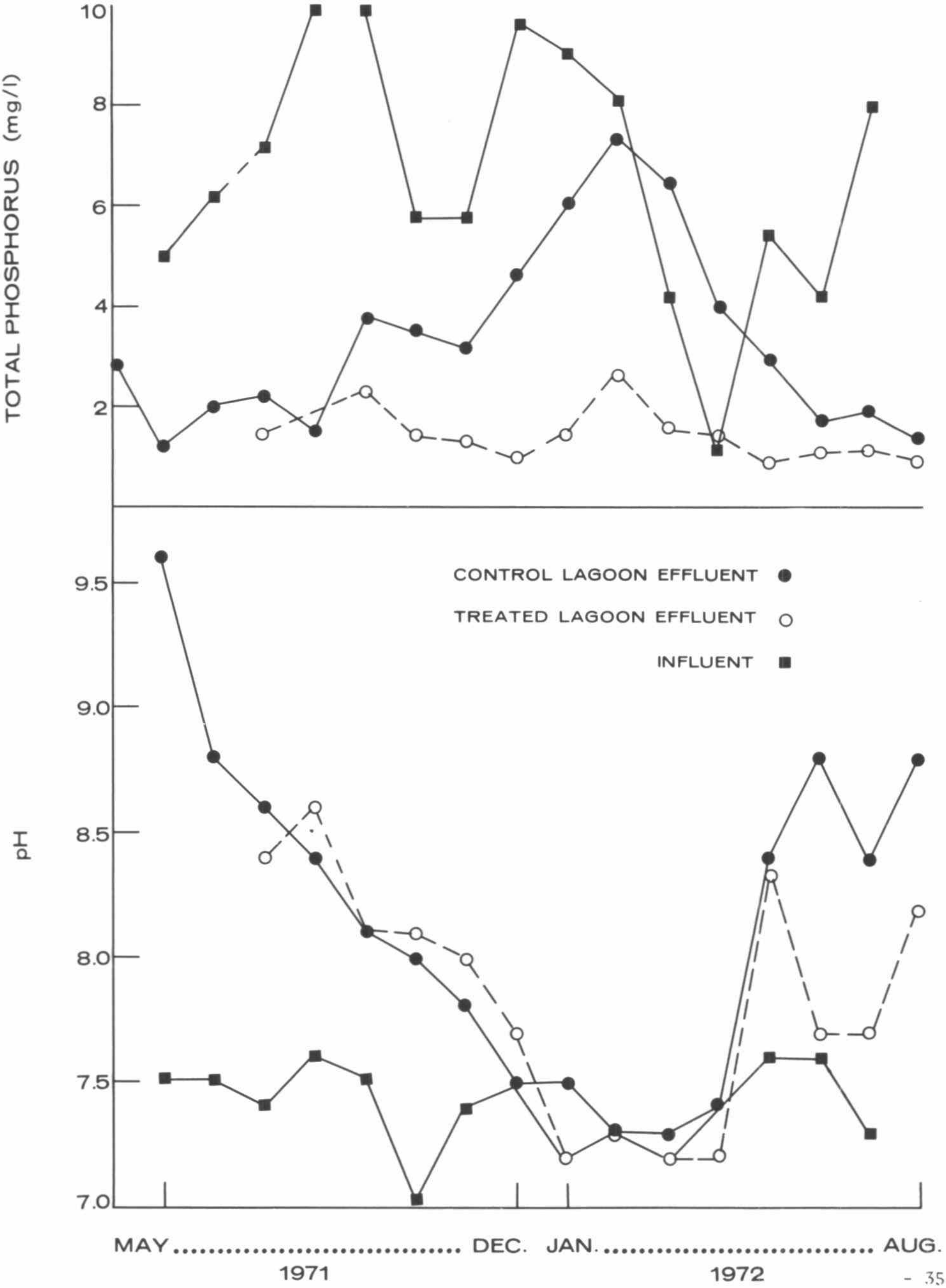


FIGURE 13 PERFORMANCE OF FULL-SCALE LAGOONS AT SHELBOURNE
ALUM DOSAGE 200 mg/l
MONTHLY AVERAGES CALCULATED FROM OME DATA



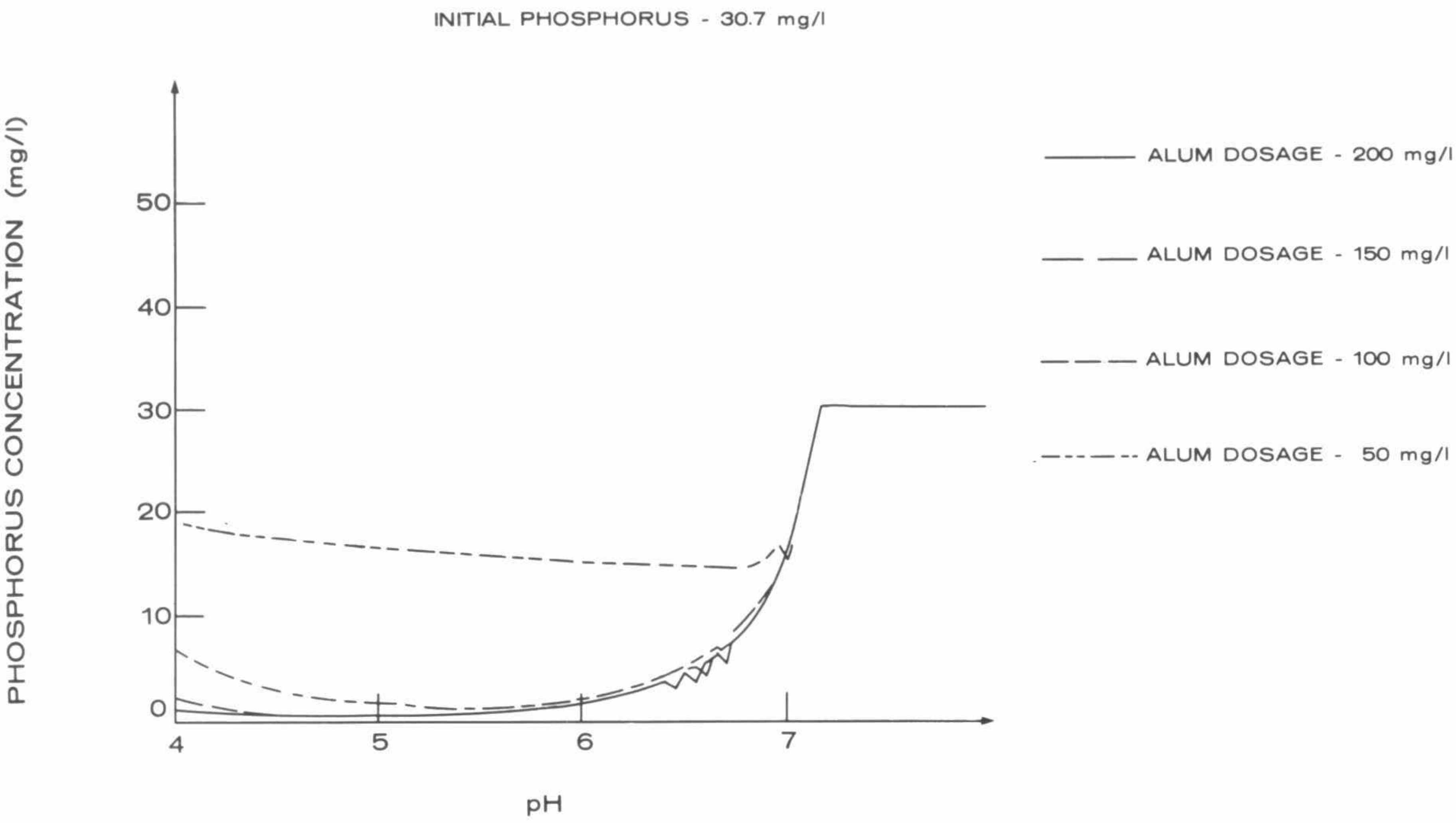


FIGURE 14. COMPUTED EFFECT OF pH ON RESIDUAL PHOSPHORUS

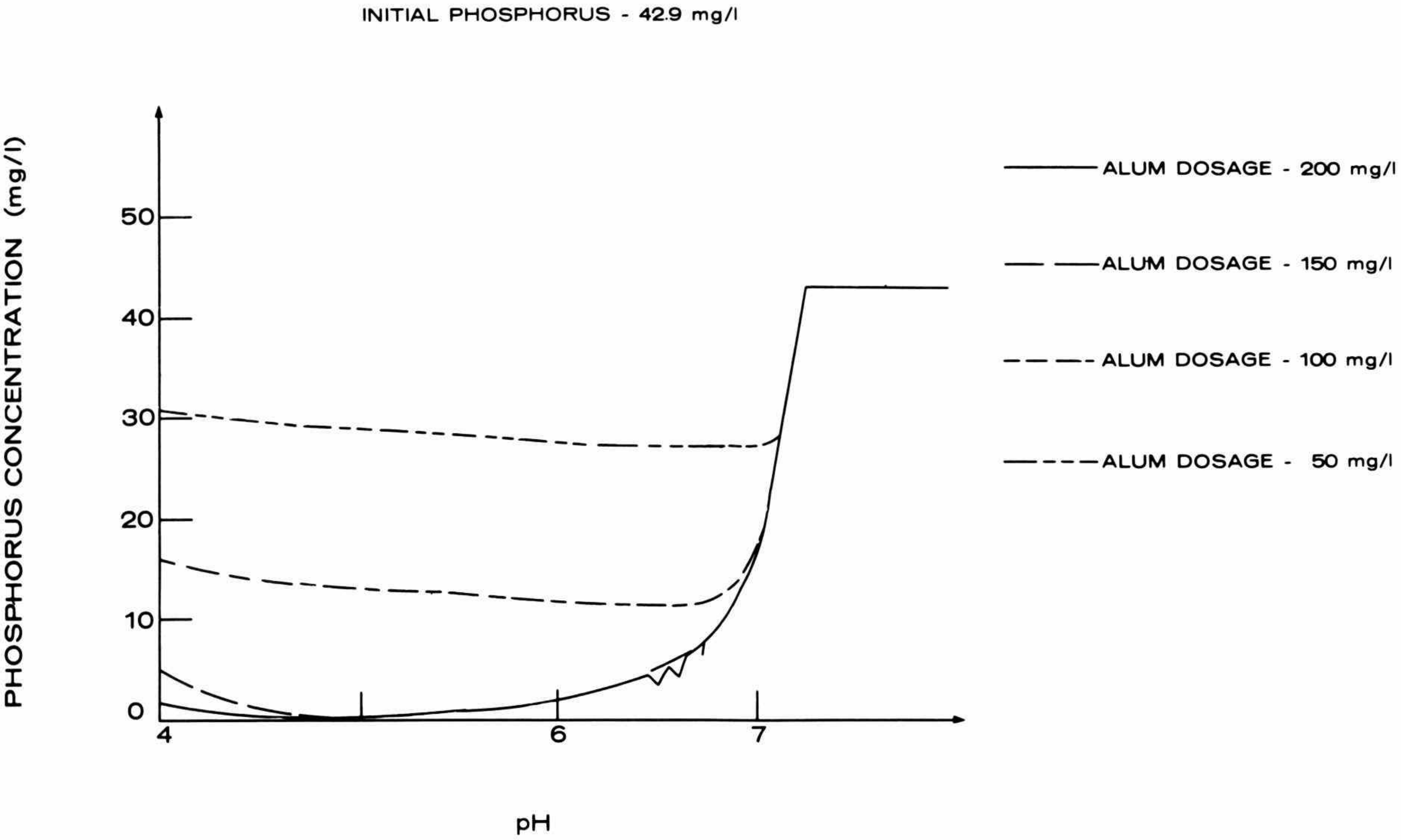


FIGURE 15. COMPUTED EFFECT OF pH ON RESIDUAL PHOSPHORUS

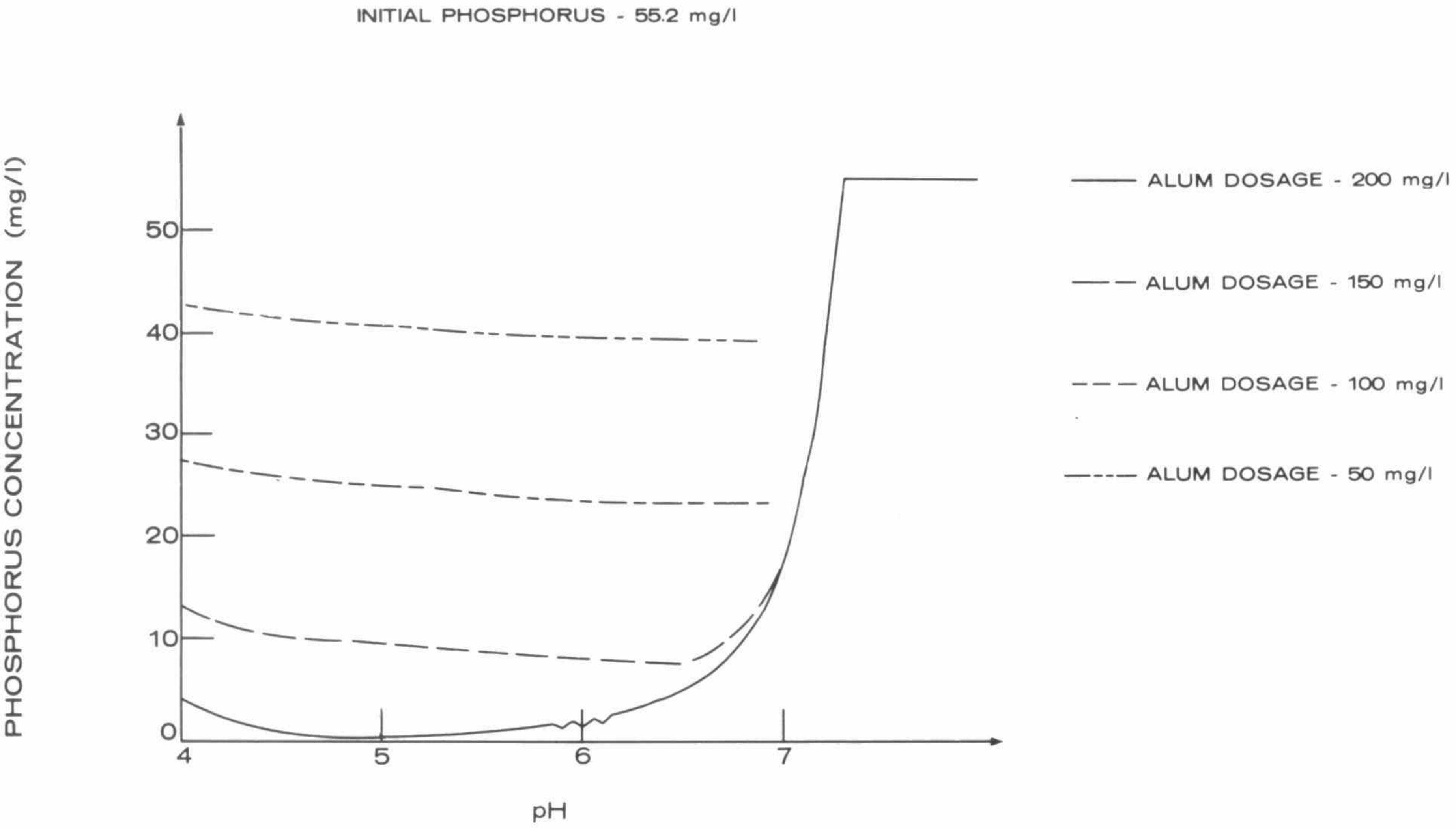


FIGURE 16. COMPUTED EFFECT OF pH ON RESIDUAL PHOSPHORUS

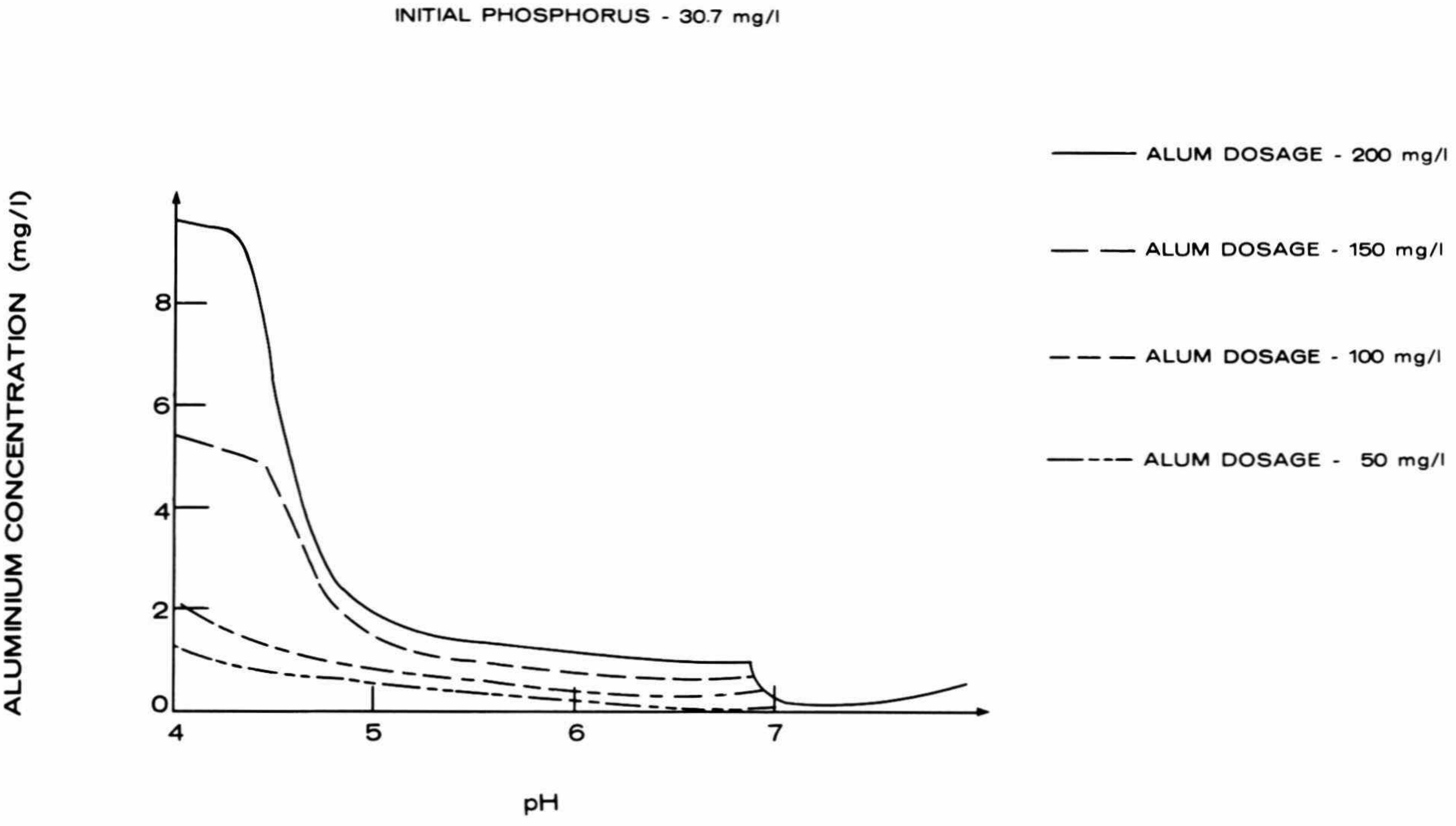


FIGURE 17. COMPUTED EFFECT OF pH ON RESIDUAL ALUMINIUM

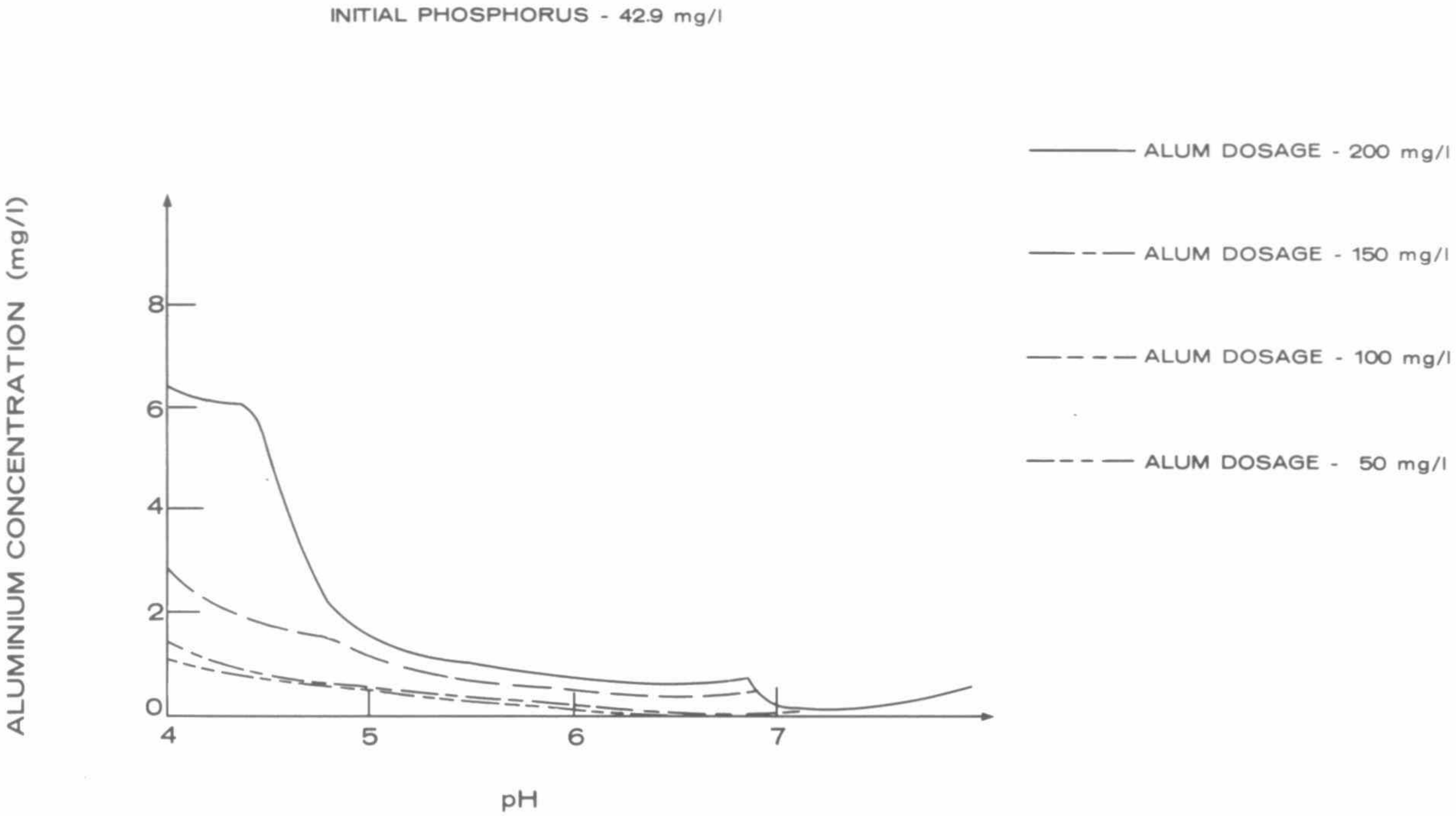


FIGURE 18. COMPUTED EFFECT OF pH ON RESIDUAL ALUMINIUM

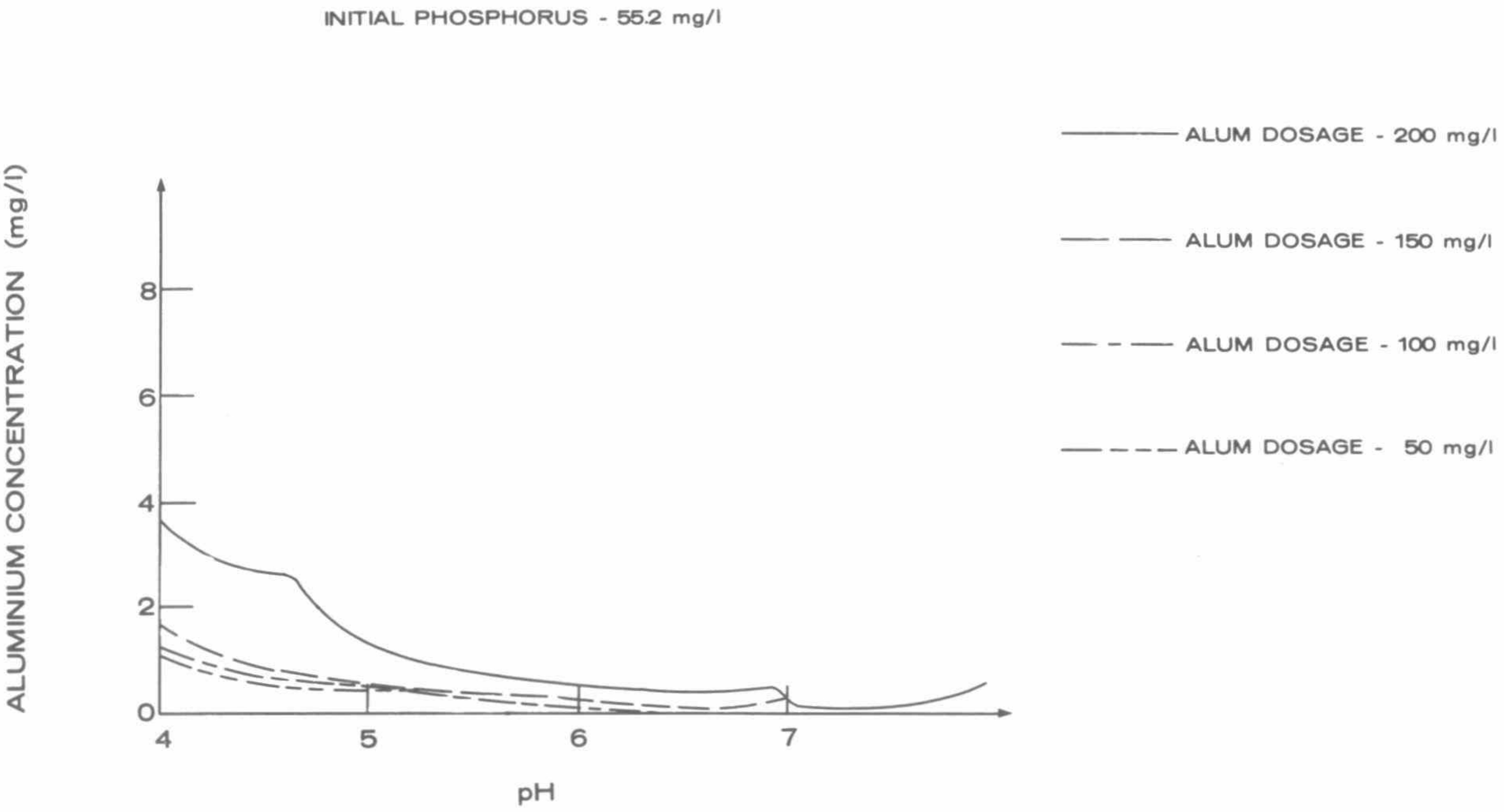


FIGURE 19. COMPUTED EFFECT OF pH ON RESIDUAL ALUMINIUM

FIGURE 20 OBSERVED EFFECT OF pH ON RESIDUAL PHOSPHORUS

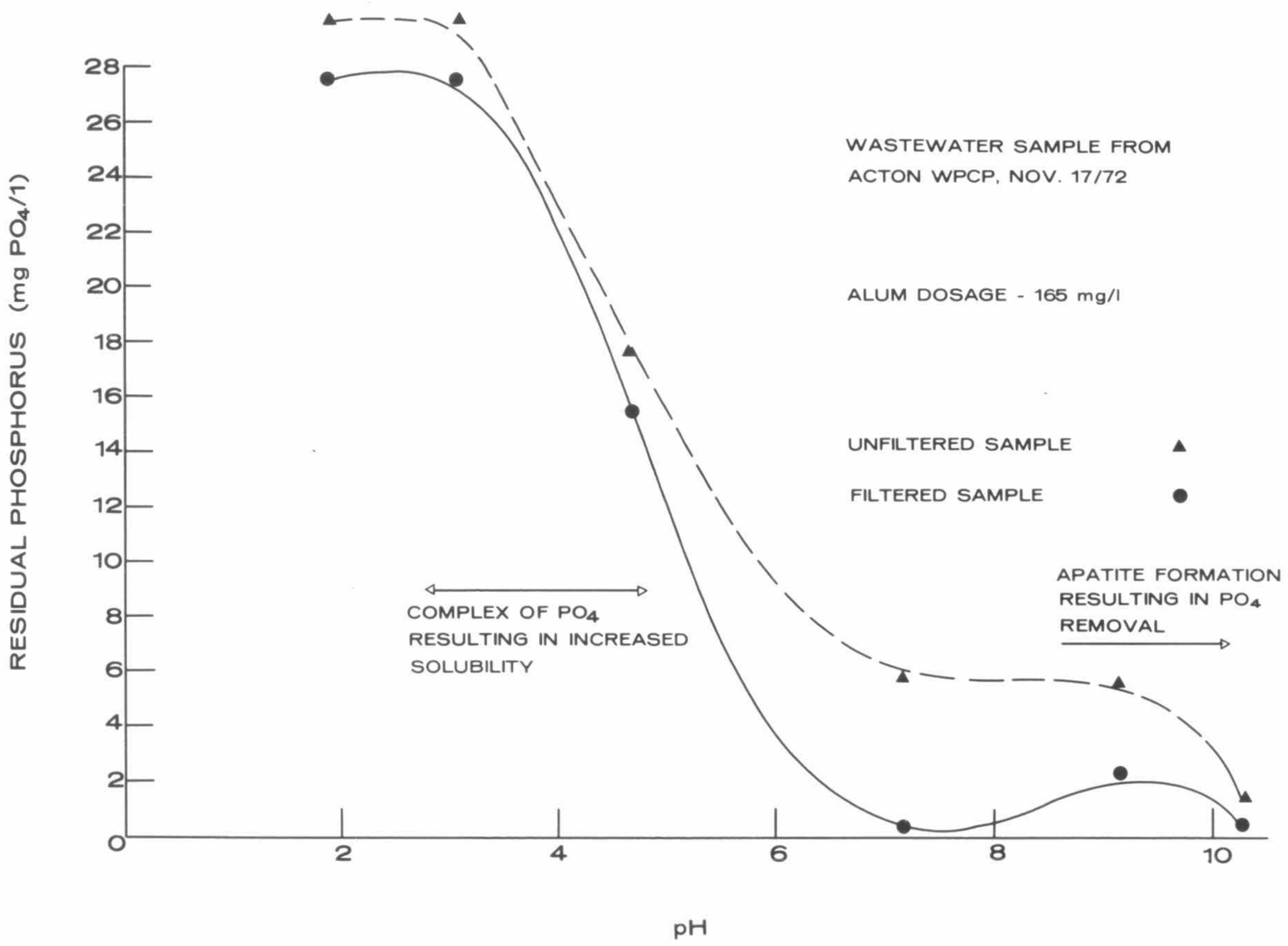


FIGURE 21 COMPARISON OF MODEL PREDICTIONS TO EXPERIMENTAL DATA

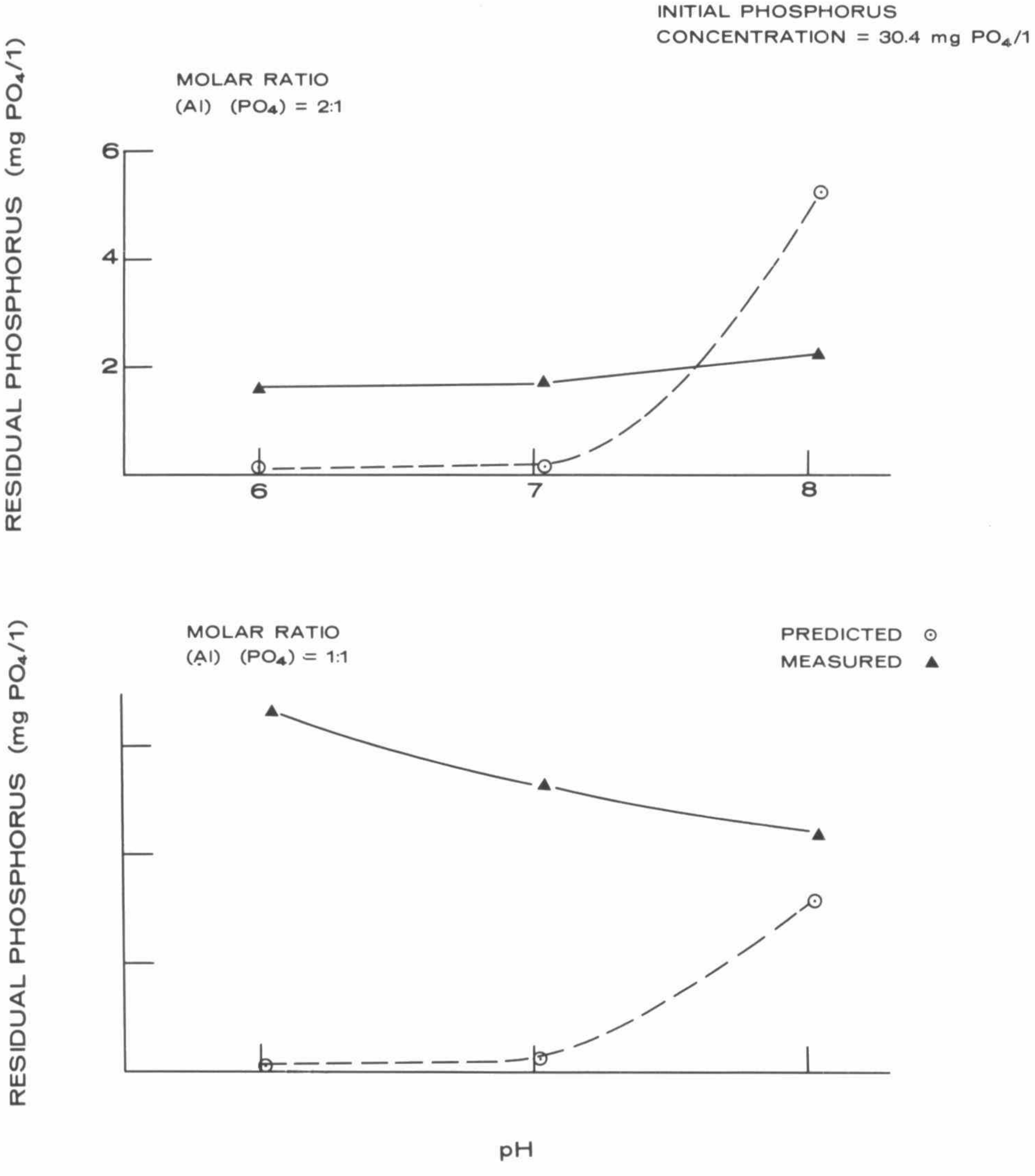
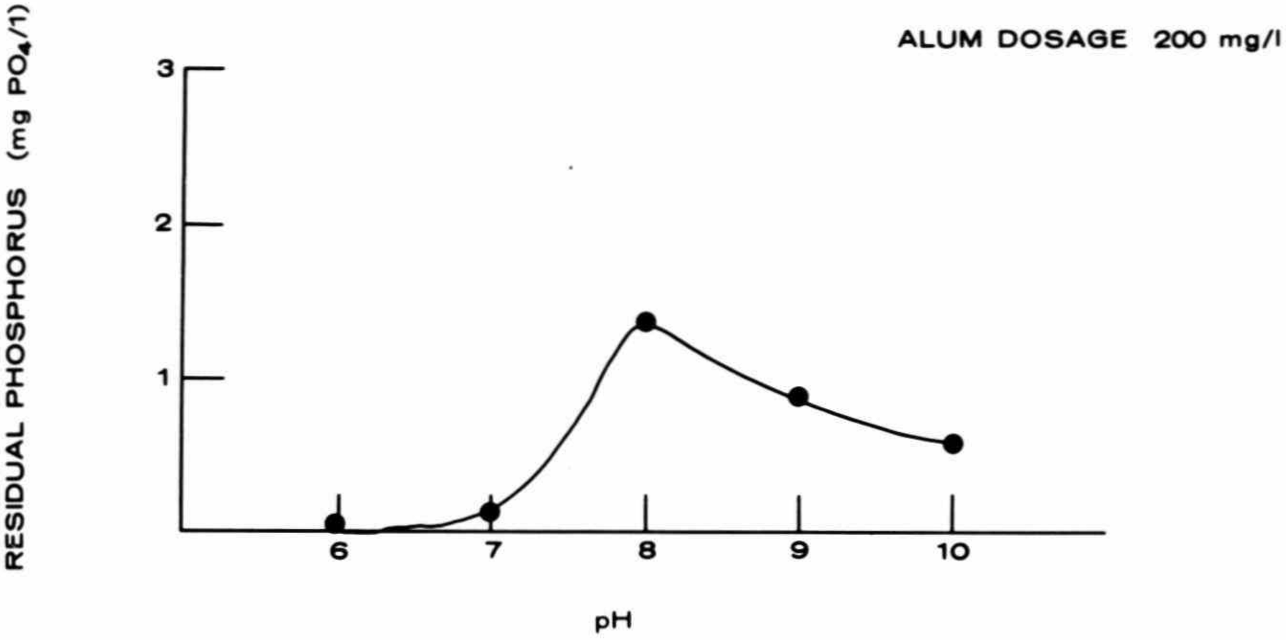


FIGURE 22 RESIDUAL PHOSPHORUS MODEL PREDICTIONS



INITIAL PO CONCENTRATION 30.4 mg PO_4/1

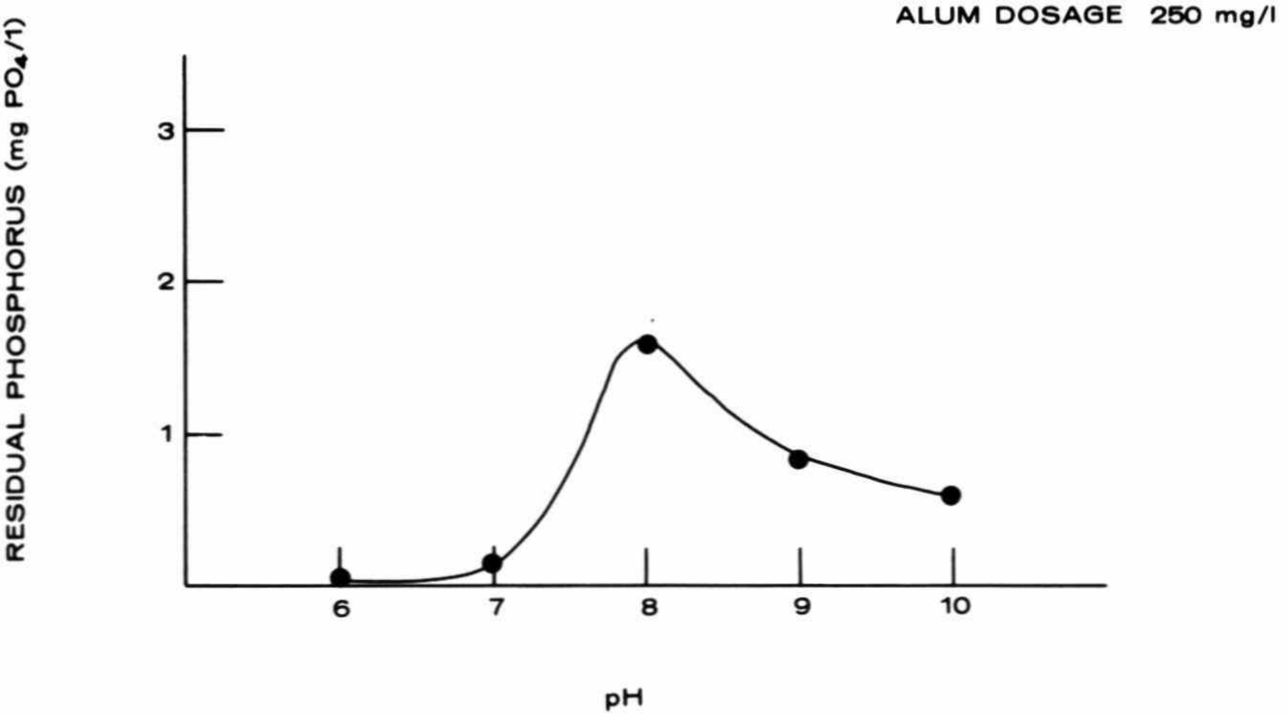
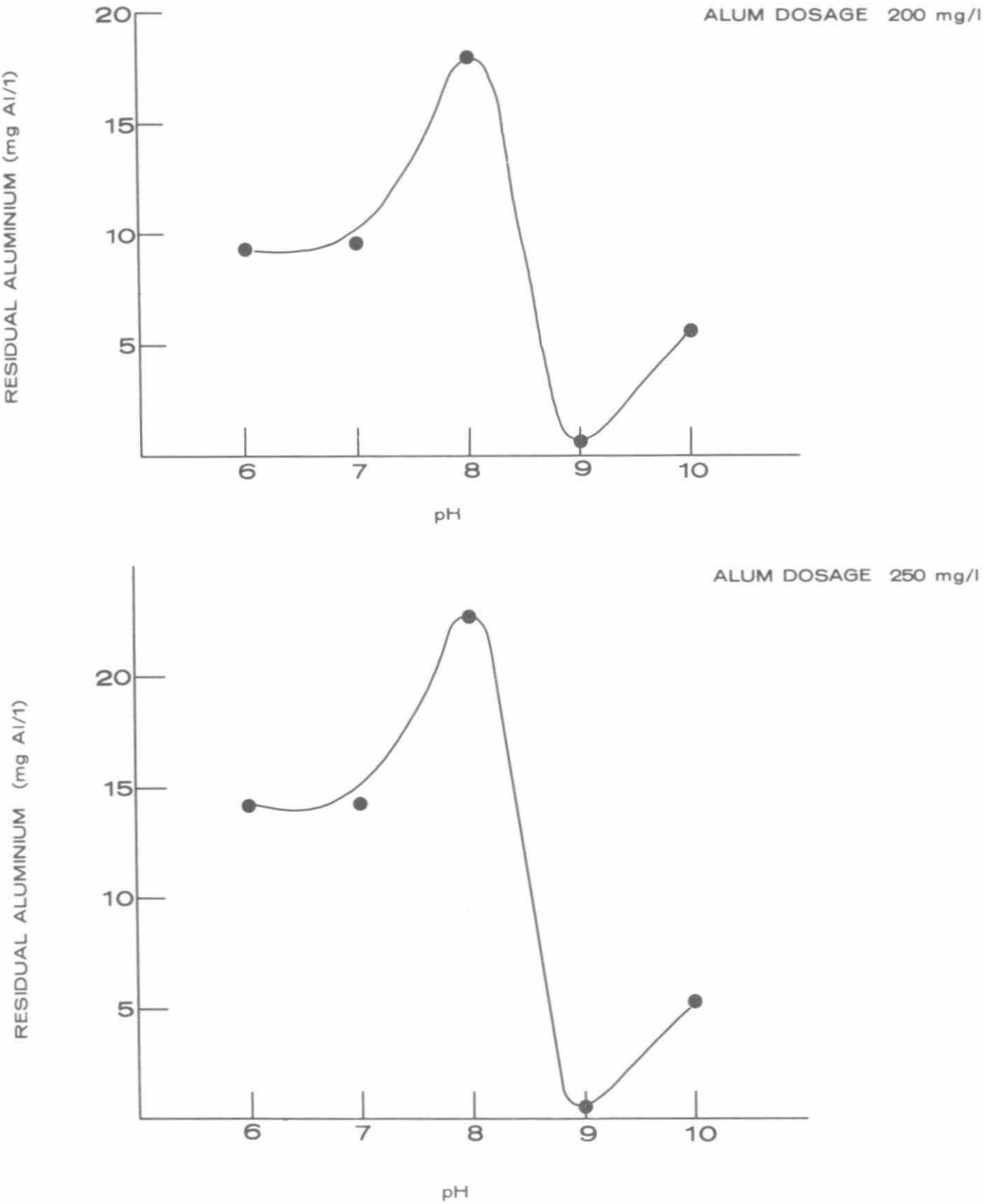


FIGURE 23 RESIDUAL ALUMINIUM MODEL PREDICTIONS



APPENDIX II

MODELING PROCEDURE

APPENDIX II

1. DESCRIPTION OF MODELING PROCEDURE

To calculate the equilibrium distribution of these 43 proposed species, an executive computer program "chemist" was used. The basic program alogarithm was developed by the Rand Corporation in Calfornia. This program has since been modified for use in describing precipitation of nutrients which occurs in wastewater treatment processes. The solution of the equilibrium problem is achieved by solving simultaneously all of the equilibrium equations representing the different reactions. Since these equilibrium expressions are non linear in form (i.e. the equilibrium reaction is expressed as the product of chemical species concentrations set equal to a constant) an iterative calculation procedure is necessary. The "chemist" program uses a calculation technique based on the linearization of the equilibrium expressions by a Taylor series approximation.

The influence of the more "inert" components particularly the the chloride, potassium and sodium ions is taken into account by considering the effect these ions have on the total ionic strength and thus, in turn, the activity or "reactive concentration". Activity coefficients as a function of the total ionic strength are calculated for each charged species at each iterative step in the solution. These coefficients as calculated by the Davis equation (3) are used to modify the actual concentration of the species to the reactive concentration.

After selection of the appropriate reactions, the input information to the computer consists of the set of equilibrium constants and the initial concentrations of the twelve ion components. The selection of equilibrium constants for the aqueous phase reactions was taken from the compiled data of Sillen (4) and Morgan (5). The reported solubility products for variscite and gibbsite were found to vary over quite a range. The reported phosphate values are 10^{-20}(6), 10^{-21}(4), 10^{-22} to $10^{-25.6}$(7). Similarly, Morgan (5) reports hydroxide solubility products at 10^{-33} and $10^{-36.3}$. In this study, the more soluble form of gibbsite was chosen as it was thought to be representative of a fresh precipitate, while the range of aluminum phosphate solubility products were tested at an alum dosage ($Al_2SO_43 \cdot 14H_2O$) of 200 mg/l and an initial alum concentration of 55.2 mg/l (as PO_4). The residual phosphate concentrations (mg PO_4/l) as predicted in this test are shown in the following table:

SOLUBILITY PRODUCT (pk value)	EQUILIBRIUM pH 4	6	8
19.9	18.6	24.2	55.1
21	4.0	2.0	55.1
22.2	8.5	0.14	55.1
25.6	.002	.00005	.03

The solubility product as reported by Sillen (4) was taken as the most representative value for use in this study.

2. MODEL REVISIONS

Experimental data were obtained on the removal of phosphorus with alum in a wastewater sample over the pH range of interest. The solubility products could then be adjusted to fit this data. Since the equilibrium model has a non-linear functional form, this approach is a modification of the parameter estimation problem for a non-linear model. This parameter estimation problem is more difficult than that of the linear case. In the latter case, the linear least-squares technique provides a set of equations which may be directly solved to obtain parameter estimates. In the former case, a trial and error solution must be used, where, in the simplest terms, a parameter estimate is made, the model response is compared to the experimental data and then a new estimate made based on the deviations between observed and predicted results.

This trial and error procedure has been formalized to some extent. These formalized procedures, called non-linear search techniques, are known as "Taylor Linearization", "Powell's Method", and "Flexible Simplex". All three were considered in solving the problem at hand. The experiments were conducted at a pH range of between 6 and 8. Below this range, it was felt that soluble aluminum phosphate complexes had an influence on the aluminum phosphate solubility but the chemistry of these reactions is not well documented. Above this range, we have observed in other cases that precipitation of phosphates results from reaction with calcium. In these cases, the wastewater influent sample in this study received no treatment other than the adjustment of solution pH with sodium hydroxide.

In estimating parameters, it was necessary to adjust the basic format of the model. The necessity arose from the problem of keeping the computation of the search techniques within practical economic limits. When the wastewater sample was acidified, dissolved inorganic carbons were removed as carbon dioxide, and therefore, the reactions in which the carbonate ion participated were removed. The reactions involving calcium and magnesium ions were also removed to simplify the model. The model was now based upon the reaction sets of the aluminum hydrolysis and phosphate acid dissociation. After this simplification each stage of the search (i.e., testing one set of parameter estimates against the experimental data) required 10 seconds of computation time. At least 100 steps were required to obtain reasonable parameter estimates.

For the first step only the solubility product of aluminum phosphate was considered to vary. "The Taylor Linearization" technique failed. The solution became unstable. This occurrence is common when the original parameter estimates are far removed from the true values. It was possible to obtain estimates of this solubility product which caused the model to predict phosphorus removals at excessive pH levels, but the removals predicted at lower pH values were much too low. The "Powell" and "Flexible Simplex Routine" proved to be equally as efficient in this case.

In the second step both the solubility products were considered to vary in the search routine. The "Taylor Linearization" technique again proved unstable, while the "Flexible Simplex" routine seemed to converge upon a solution the most efficiently of the three. Again, estimates were obtained which resulted in the model predicting phosphate precipitation at pH values of 8. However, the model predicted that excess aluminum (i.e., that not precipitated with phosphate) would remain in solution as soluble complexes. This is contrary to observed phenomena, as aluminum residuals are always low in this pH range, even when added in excess of the phosphate requirements. This problem was believed to have resulted from changing the solubility product of the aluminum hydroxide while leaving the equilibrium constants of the hydroxide complexes constant.

The last step was to increase the number of search variables. Morgan (5) concluded from his studies that the most important hydorxide complexes to consider in describing the solubility of freshly precipitated aluminum hydroxide are the polymeric complex $Al_{13}OH_{34}^{5+}$ in an acidic solution and $Al(OH)_4^-$ in a basic solution. Four search variables were considered, the two solubility products and the two hydrolysis constants. The following estimates were obtained for these parameters and are compared to the values originally quoted in the literature. These estimates were obtained after 100 evaluations using the "Flexible Simplex" routine. With these last parameter estimates, excess aluminum was precipitated as the hydroxide.

Parameter Estimates

Species	$AlPO_{4(s)}$	$Al(OH)_{3(s)}$	$Al_{17}OH_{34}^{5+}$	$AlOH_4^-$
Estimated Value*	20.8	30.1	350	30.0
Literature Value	20 - 25	33 - 36	371	33.7

* Negative logarithm

APPENDIX III

ANALYTICAL METHOD FOR PHOSPHORUS DETERMINATION

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ANALYTICAL METHOD FOR PHOSPHORUS DETERMINATION

A. Determination of Total Phosphorus (acid-hydroysable)

(1) A suitable aliquot of thoroughly mixed sample (depending on the expected phosphorus concentration) is measured out into a beaker and diluted to approximately 60 ml.

(2) 2 drops of phenolphthalein indicator are added. If red colour develops, strong acid solution (600 ml concentrated H_2SO_4 plus 4 ml concentrated HNO_3 diluted to 1 litre) is added to just discharge the colour. Boiling chips and an additional 0.5 ml of strong acid solution are added, and the beaker is covered with a watch glass and boiled for 90 minutes at $400^{o}F$. The volume of the solution is maintained between 30 and 60 ml.

(3) The boiled solution is cooled. NaOH of known normality (i.e. 6N) is added until the solution turns pink, and it is then titrated with dilute H_2SO_4 until the colour is just eliminated.

(4) The neutralized solution is transferred quantitatively to a 100 ml volumetric flask and made up to volume.

(5) 4 ml of Ammonium Molybdate solution,
($25gm (NH_4)_6 MO_7 O_{24} \cdot 4H_2O$ plus 280 ml concentrated H_2SO_4 in 1 litre)
and 6 drops Stannous Chloride solution,
(2.5 gm $SnCl_2 \cdot 2H_2O$ in 100 ml glycerol) are added and the colour developed for 10 minutes.

(6) The absorbance is read on a Spectrophotometer at a wave length of 690 mμ.

(7) The concentration of total phosphorus is read from the calibration curve.

B. Determination of Total Soluble Phosphorus (filtrable)

The sample is filtered through Cartorius membrane filters and a suitable aliquot of filtrate is taken for determination. Then the procedure outlined under A. is followed.

C. Determination of Ortho-Phosphorus

(1) A suitable aliquot of thoroughly mixed sample is measured out in 100 ml volumetric flask, pH adjusted to neutral, if necessary, and made up to volume.

(2) 4 ml of Ammonium Molybdate solution,
(25gm$(NH_4)_6$ $MO_7O_{24}\cdot 4H_2O$ plus 280 ml concentrated H_2SO_4 in 1 litre)
and 6 drops Stannous Chloride solution,
(2.5 gm $SnCl_2\cdot 2H_2O$ in 100 ml glycerol) are added and the colour developed for 10 minutes.

(3) The absorbance is read on a Spectrophotometer at a wave length of 690 mμ.

(4) The concentration of ortho phosphorus is read from the calibration curve.

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